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Short Note

1,4-Diiodotetrafluorobenzene 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole <1/1>

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Abstract: The reactivity of 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole (**L1**) with 1,4-diiodotetrafluorobenzene (**1,4-DITFB**) was explored and the halogen-bonded 1:1 co-crystal (**1**) was successfully isolated and structurally characterized.

Keywords: dipyridyl-1,2-4-thiadiazole; polypyridyl donors; halogen bonding; SC-XRD

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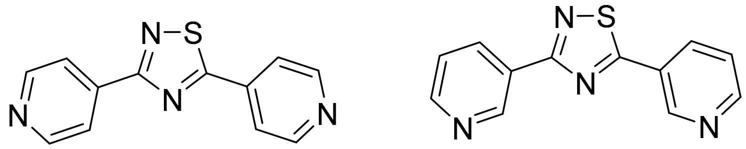
1. Introduction

1,2,4-Thiadiazoles have been recognized as effective scaffolds in medicinal chemistry, since many derivatives are biologically active and very promising candidates in drug design [1]. Inspired by Cefozopran [2], the first 1,2,4-thiadiazole derivative to enter the market as an antibiotic, extensive synthetic efforts led to the isolation of numerous 1,2,4-thiadiazoles with potential biomedical applications, such as high cytotoxicity against human myeloid leukemia cells [3], inhibitors of Factor XIIIa in the blood coagulation process [4], neuroprotectors, [5] and in the treatment of Alzheimer's disease [6]. The synthesis of 1,2,4-thiadiazoles is typically achieved starting from thioamides, whose oxidation is followed by cyclization, and several methods have been reported using a range of oxidants and reaction solvents [7,8]. A valid protocol reported the use of alcoholic thioamide solutions, which can be easily oxidized by molecular dihalogens, leading to the corresponding thiadiazole in good yields [9].

1,2,4-Thiadiazoles featuring pyridyl substituents, such as 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole (**L1**) and 3,5-di-(pyridin-3-yl)-1,2,4-thiadiazole (**L2**) (Scheme 1), have been successfully used as building blocks in supramolecular chemistry by exploring their reactivity towards metal ions in the preparation of coordination polymers and polygons [10,11]. The versatility of donors **L1** and **L2** as supramolecular synthons became evident when their reactivity towards dihalogens, interhalogens, and other halogenated derivatives was investigated [12,13]. In this regard, the reaction of **L1** and **L2** with dihalogens and interhalogens was previously reported by our research group [12], and the self-assembly outcomes are summarized in Scheme 1. The results showed that donors **L1** and **L2** can give either Charge-Transfer (CT) adducts or salts with variable degrees of N-protonation (e.g., HL^+, H_2L^{2+}) depending on the solvent polarity and the experimental setup (Scheme 1). The reaction of **L2** with diiodine in CH_2Cl_2 resulted in the bis-adduct $\mathbf{L2}\cdot 2I_2$ with a short N$\cdots$I bond distance (2.505 Å) and a linear N$\cdots$I–I fragment as typically observed in CT-adducts. Notably, the reaction of **L1** with diiodine under the same experimental conditions did not produce a crystalline product and its nature as $\mathbf{L1}\cdot 2I_2$ was established by microanalytical determinations and Raman spectroscopy [12].



L1 **L2**

		Ref.		Ref.
CT adducts	**L1**·$2I_2$ *	[12] *	**L2**·$2I_2$	[12] (WEDHUK)
Ionic compounds	(H**L1**$^+$)(IBr_2^-)	[12] (WEDHOE)	(H**L2**$^+$)(IBr_2^-)	[12] (WEDHEU)
	(H**L1**$^+$)(I_3^-)	[12] (WEDHIY)	(H**L2**$^+$)(I_3^-)	[12] (WEDGUJ)
	(H_2**L1**$^{2+}$)(I_3^-)$_2$·$2H_2O$	[13] (XEKTAM)	(H**L2**$^+$)(I_5^-)	[12] (WEDHAQ)
	(H_2**L1**$^{2+}$)$_2$($Bi_8I_{28}^{4-}$)·$4CH_3CN$	[13] (XEKVIW)	(H**L2**$^+$)(I^-)·$4CH_3CN$	[13] (XEKTEQ)
	[(H_2**L1**$^{2+}$)(H**L1**$^+$)]($Bi_2I_9^{3-}$)·$3H_2O$	[13] (XEKVOC)	(H_2**L2**$^{2+}$)(I_3^-)$_2$·**L2**	[13] (XEKTIU)
			(H_2**L2**$^{2+}$)(I^-)$_2$·**L2**·$2CHI_3$	[13] (XEKTOA)
			(H_2**L2**$^{2+}$)$_2$($Bi_4I_{16}^{4-}$)·$2CH_3CN$·$2I_2$	[13] (XEKVUI)
			(H_2**L2**$^{2+}$)$_2$($Bi_6I_{22}^{4-}$)·$2CH_3OH$	[13] (XEKWAP)

* Note: **L1**·$2I_2$ was not structurally characterized.

Scheme 1. CT adducts and ionic compounds isolated from the reactions between N-donors **L1** and **L2** and halogenated species. Refcodes are given in parentheses.

The role of the solvent becomes crucial when considering the products obtained from the reactions between **L1** or **L2** and I_2 or IBr in ethyl alcohol, where the following ionic compounds were obtained: (H**L1**$^+$)(IBr_2^-), (H**L1**$^+$)(I_3^-), (H**L2**$^+$)(IBr_2^-), (H**L2**$^+$)(I_3^-), (H_2**L2**$^{2+}$)(I_3^-)$_2$·**L2,** (H**L2**$^+$)(I_5^-) (Scheme 1) [12,13]. These structures share cations H**L1**$^+$ or H**L2**$^+$ with only one of the two pyridyl nitrogen atoms being protonated, resulting in the formation of head-to-tail polymeric arrays held by $NH^+ \cdots N$ hydrogen bonds ($d_{N\cdots N}$ distances up to 2.770 Å), whose motif is shaped by the geometrical features of the former donors: wavy chains for cations H**L1**$^+$ and either helices or zig-zag chains in the case of cations H**L2**$^+$ [12]. The only exception among these ionic compounds is represented by (H_2**L2**$^{2+}$)(I_3^-)$_2$·**L2,** where the donor **L2** appears in both the neutral and the doubly charged H**L2**$^{2+}$ form.

When acetonitrile was used as a solvent and the donors **L1** and **L2** were reacted with I_2, (H_2**L1**$^{2+}$)(I_3^-)$_2$·$2H_2O$ and (H**L2**$^+$)(I^-)·$4CH_3CN$ were isolated [13]. Moreover, the reaction of **L2** with I_2 in an iodoform/acetone mixture produced compound (H_2**L2**$^{2+}$)(I^-)$_2$·**L2**·$2CHI_3$ [13]. To further investigate the reactivity of **L1** and **L2** toward dihalogens, Pennington and coworkers introduced bismuth triiodide as a building block, producing self-assembled salts with formula (H_2**L1**$^{2+}$)$_2$($Bi_8I_{28}^{4-}$)·$4CH_3CN$, [(H_2**L1**$^{2+}$)(H**L1**$^+$)]($Bi_2I_9^{3-}$)·$3H_2O$, (H_2**L2**$^{2+}$)$_2$($Bi_4I_{16}^{4-}$)·$2CH_3CN$·$2I_2$, and (H_2**L2**$^{2+}$)$_2$($Bi_6I_{22}^{4-}$)·$2CH_3OH$, whose crystal structures show **L1** and **L2** in their mono- or diprotonated forms along with four unusual polyiodobismuthate counterions [13].

On the contrary, the interaction of **L1** and **L2** with the halogen atoms of halo-organic compounds has not yet been reported. This interaction falls into the realm of halogen bonding because it involves a halogen atom acting as an electrophilic site and the lone pair of a pyridine nitrogen atom as a nucleophilic site [14–16]. Following our interest in the study of σ-hole interactions between halogen-rich compounds and pyridine tectons [17,18], we report here on the synthesis and characterization of the novel halogen-bonded 1:1 co-crystal (**1**) formed between **L1** and 1,4-diiodotetrafluorobenzene (**1,4-DIFTB**). In this halo-organic compound, the σ-hole effect for the iodide atoms is enhanced by the presence of the four electronegative fluorides, and numerous co-crystals formed by the halogen bonding between **1,4-DIFTB** and pyridine donors can be found in the literature [14,19–23].

2. Results

The slow evaporation of a chloroform solution of **L1** and **1,4-DITFB** in 1:1 molar ratio at room temperature afforded colorless crystals, established by means of X-ray diffraction analysis as a 1:1 halogen-bonded co-crystal with formula **L1·1,4-DITFB** (compound **1**; Figure 1)**.** Compound **1** crystallizes in the triclinic space group *P*−1 with two units in the unit cell (see Table S1 for structural data and refinement parameters).

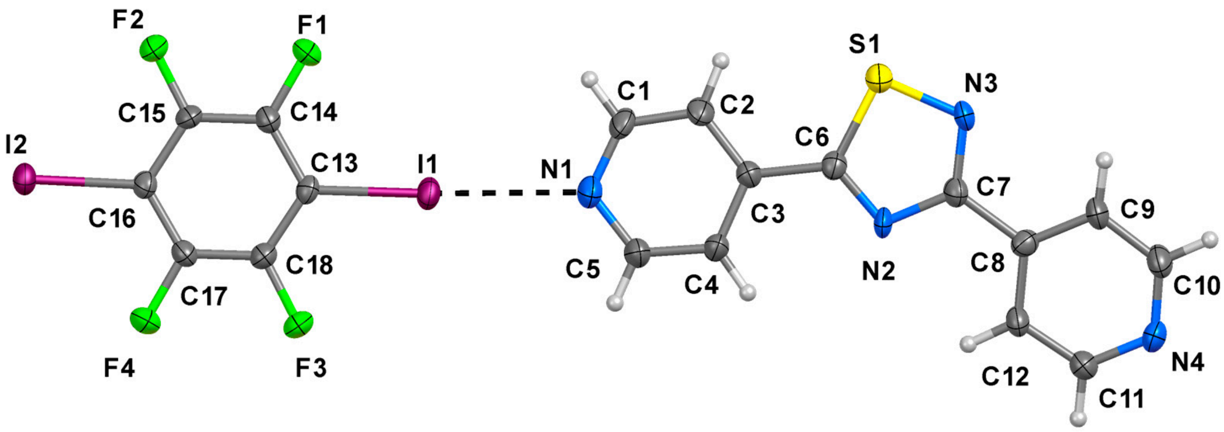


Figure 1. X-ray crystal structure of compound **1** with the numbering scheme adopted. Displacement ellipsoids were drawn at the 50% probability level.

Crystal data for compound **1**: $C_{18}H_8F_4I_2N_4S$, (Mr = 642.14 g mol^{-1}) triclinic, *P*−1, a = 5.6690(4) Å, b = 12.3300(9) Å, c = 14.1339(9) Å, α = 91.644(6), β = 96.314(6)°, γ = 92.400(6)°, V = 980.54(12) Å^3, T = 173(2) K, Z = 2, ρ_{calc} = 2.175 g/cm^3, μ(Mo $K\alpha$) = 3.363 mm^{-1}. The final R_1 was 0.0333 [$F^2 \geq 2\ \sigma(F^2)$], wR_2 was 0.0960 (all data), and the GooF = 1.043.

The **1,4-DITFB** molecules interact with **L1** to form neutral adducts at both N-pyridyl atoms with $d_{N\cdots I}$ distances of 2.801(5) and 2.947(4) Å and C–I···N angles of 177.4(2) and 168.3(2)° for N1···I1 and N4···I2^{i}, respectively (entries *a* and *b* in Figure 2; ^{i} = 2 + x, −1 + y, −1 + z; Tables S2 and S3). These values are similar to the average N···I value of 2.9(2) Å retrieved from the CSD database (version 5.43, three updates) for the structurally characterized compounds in which **1,4-DITFB** interacts with pyridyl-based donors (the search was constrained to N···I distances up to the sum of the atomic van der Waals radii: 3.53 Å).

The resulting $(\mathbf{L1{\cdot}1,4\text{-}DITFB})_\infty$ 1D-chains propagate approximately along the [$\bar{2}$11] direction and pack into 2D sheets via weak C–H···F interactions (entries c–e in Figure 2 and Table 1) [23]. The FT-IR spectrum (Figure S1) recorded for compound **1** showed a shift towards lower frequency of the ν(C–I) stretching mode from 760 to 748 cm^{-1} on passing from free **1,4-DITFB** to the co-crystal, as a consequence of the halogen bonding between the two species [14].

Table 1. Compound **1** intermolecular interactions.

	C–I···N	$d_{C–I}$ (Å)	$d_{I\cdots N}$ (Å)	$\alpha_{C–I\cdots N}$ (°)	
a	C13–I1···N1	2.101(5)	2.801(5)	177.4(2)	
b	C16^{i}–I2^{i}···N4	2.092(5)	2.947(4)	168.3(2)	
	C–H···F	$d_{C–H}$ (Å)	$d_{H\cdots F}$ (Å)	$d_{C\cdots F}$ (Å)	$\alpha_{C–H\cdots F}$ (°)
c	C2–H2···F2^{ii}	0.95	2.450	3.307(6)	150
d	C4–H4···F3^{iii}	0.95	2.607	3.142(6)	122
e	C5–H5···F3^{iii}	0.95	2.505	3.111(6)	116

Symmetry codes: ^{i} = 2 + x, −1 + y, −1 + z; ^{ii} = 1 − x, 2 − y, 1 − z; ^{iii} = −x, 1 − y, 1 − z.

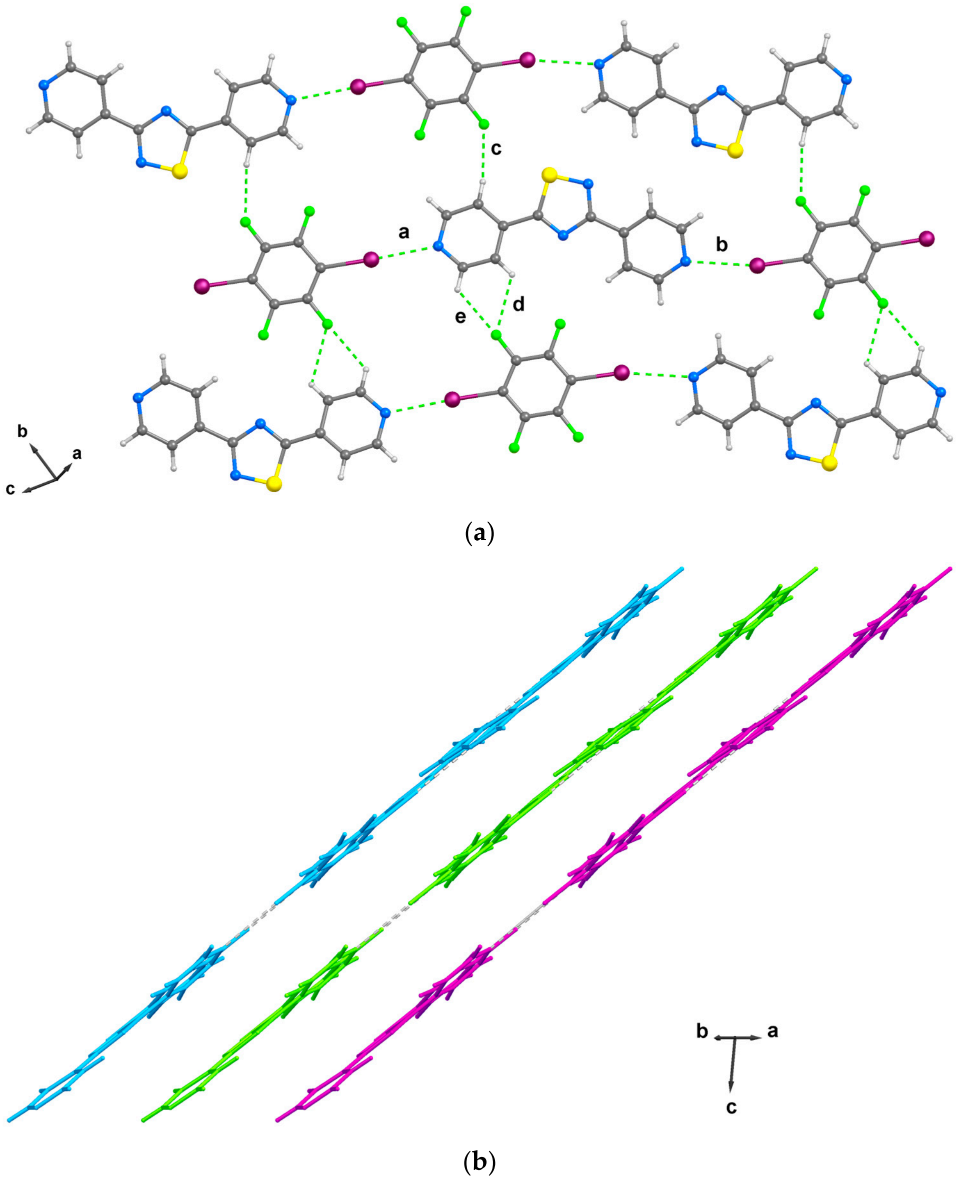


Figure 2. Partial view of the crystal packing of **1** showing (**a**) a single layer with the relevant intermolecular interactions **a**–**e** are labelled according to Table 1, and (**b**) adjacent layers viewed along the [110] direction.

3. Materials and Methods

3.1. General

L1 was synthesized according to a method in the literature [9]. **1,4-DIFTB** and chloroform were purchased from Merck and used without any further purification. Elemental analysis determinations were performed with a Perkin Elmer EA CHN elemental analyzer. The FT-IR spectra (4000–400 cm^{-1}) were recorded on KBr pellets on a Thermo Nicolet 5700 spectrometer. Melting point determination was performed on a FALC mod. C apparatus. Single crystal X-ray diffraction data were collected at 173 K on a Rigaku SCX mini diffractometer using graphite monochromated Mo $K\alpha$ radiation (0.71073 Å). Data collection and processing were carried out using CrysAlisPro [24]. The structure was solved with the ShelXT [25] solution program using dual methods and the model was refined using full matrix least squares minimization on F^2 with ShelXL [26] 2018/3. The crystal was found to be a non-merohedral twin and the model was refined as a two-component twin. Olex2 1.5 [27] was used as the graphical interface.

3.2. Preparation of **L1·1,4-DITFB** (**1**)

L1 (12.0 mg; 5.00 × 10^{-5} mol) and **1,4-DITFB** (20.1 mg; 5.00 × 10^{-5} mol) were dissolved in chloroform (5 mL) and the mixture was stirred at room temperature for 20 min. The resulting solution was filtered through a PTFE filter and the solvent allowed to evaporate slowly to afford compound **1** as colorless crystals suitable for X-ray diffraction analysis (10.8 mg; 1.68 × 10^{-5} mol; 34%). Elemental analysis calcd (%) for $C_{18}H_8F_4I_2N_4S$: C 32.67, H 1.26, N 8.73. Found: C 31.88, H 0.66, N 8.21. M.p. = 186 °C. FT-IR (KBr, 4000–400 cm^{-1}): 1599 m, 1458 vs, 1410 s, 1335 m, 1290 m, 1207 m, 1124 m, 1063 m, 995 m, 939 s, 825 ms, 748 m, 733 ms, 712 ms, 677 m, 636 ms, 505 m, 474 w, 422 w cm^{-1}(Figure S1).

4. Conclusions

The halogen-bonded co-crystal (**1**) was obtained by the self-assembly of 3,5-di-(pyridin-4-yl)-1,2,4-thiadiazole (**L1**) and 1,4-diiodotetrafluorobenzene (**1,4-DITFB**) in chloroform. The crystal structure of **1**, determined by means of crystallographic tools, corresponds to the formulation **L1**·**1,4-DITFB**. A comparison between the FT-IR spectra of **1** and **1,4-DITFB** provided further evidence for the halogen bonding between the two building blocks.

Supplementary Materials: The following supporting information is available online. Figure S1: Solid-state FT-IR spectrum of compound **1** (500–3500 cm^{-1}, KBr pellet); Table S1: Crystal data and structure refinement parameters for compound **1**; Tables S2: Bond lengths (Å) for compound **1**; Tables S3: Bond angles (°) for compound **1**.

Author Contributions: Conceptualization and writing (original draft): E.P., M.C.A.; Data analysis and presentation of results: M.C.A., E.P. and A.P., M.C.A., V.L. and F.I. are experts in the field of halogen bonding and extensively investigated the reactivity of L1 towards various halogenated species. A.M.Z.S., J.D.W. and C.L.C.-W. performed the XRD analysis of compound **1**. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Crystallographic data were deposited at CCCD (CIF deposition number 2332380).

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Frija, L.M.T.; Pombeiro, A.J.L.; Kopylovich, M.N. Building 1,2,4-Thiadiazole: Ten Years of Progress. *European J. Org. Chem.* **2017**, *2017*, 2670–2682. [CrossRef]
2. Iizawa, Y.; Okonogi, K.; Hayashi, R.; Iwahi, T.; Yamazaki, T.; Imada, A. Therapeutic Effect of Cefozopran (SCE-2787), a New Parenteral Cephalosporin, against Experimental Infections in Mice. *Antimicrob. Agents Chemother.* **1993**, *37*, 100–105. [CrossRef] [PubMed]
3. Romagnoli, R.; Baraldi, P.G.; Carrion, M.D.; Cruz-Lopez, O.; Preti, D.; Tabrizi, M.A.; Fruttarolo, F.; Heilmann, J.; Bermejo, J.; Estévez, F. Hybrid Molecules Containing Benzo[4,5]Imidazo[1,2-d][1,2,4]Thiadiazole and α-Bromoacryloyl Moieties as Potent Apoptosis Inducers on Human Myeloid Leukaemia Cells. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 2844–2848. [CrossRef] [PubMed]
4. Leung-Toung, R.; Tam, T.F.; Wodzinska, J.M.; Zhao, Y.; Lowrie, J.; Simpson, C.D.; Karimian, K.; Spino, M. 3-Substituted Imidazo[1,2-d][1,2,4]-Thiadiazoles: A Novel Class of Factor XIIIa Inhibitors. *J. Med. Chem.* **2005**, *48*, 2266–2269. [CrossRef] [PubMed]
5. Perlovich, G.L.; Proshin, A.N.; Volkova, T.V.; Petrova, L.N.; Bachurin, S.O. Novel 1,2,4-Thiadiazole Derivatives as Potent Neuroprotectors: Approach to Creation of Bioavailable Drugs. *Mol. Pharm.* **2012**, *9*, 2156–2167. [CrossRef] [PubMed]
6. Martinez, A.; Alonso, M.; Castro, A.; Pérez, C.; Moreno, F.J. First Non-ATP Competitive Glycogen Synthase Kinase 3 β (GSK-3β) Inhibitors: Thiadiazolidinones (TDZD) as Potential Drugs for the Treatment of Alzheimer's Disease. *J. Med. Chem.* **2002**, *45*, 1292–1299. [CrossRef] [PubMed]
7. Cashman, J.R.; Hanzlik, R.P. Oxidation and Other Reactions of Thiobenzamide Derivatives of Relevance to Their Hepatotoxicity. *J. Org. Chem.* **1982**, *47*, 4645–4650. [CrossRef]
8. Castro, A.; Castaño, T.; Encinas, A.; Porcal, W.; Gil, C. Advances in the Synthesis and Recent Therapeutic Applications of 1,2,4-Thiadiazole Heterocycles. *Bioorg. Med. Chem.* **2006**, *14*, 1644–1652. [CrossRef] [PubMed]

9. Meltzer, R.I.; Lewis, A.D.; King, J.A. Antitubercular Substances. IV. Thioamides. *J. Am. Chem. Soc.* **1955**, *77*, 4062–4066. [CrossRef]
10. Aragoni, M.C.; Arca, M.; Coles, S.J.; Crespo Alonso, M.; Coles, S.L.; Davies, R.P.; Hursthouse, M.B.; Isaia, F.; Lai, R.; Lippolis, V. Coordination Polymers and Polygons Using Di-Pyridyl-Thiadiazole Spacers and Substituted Phosphorodithioato Ni II Complexes: Potential and Limitations for Inorganic Crystal Engineering. *CrystEngComm* **2016**, *18*, 5620–5629. [CrossRef]
11. Podda, E.; Arca, M.; Coles, S.J.; Crespo Alonso, M.; Isaia, F.; Pintus, A.; Lippolis, V.; Aragoni, M.C. Supramolecular Assemblies Tailored by Dipyridyl-1,2-4-Thiadiazoles: Influence of the Building Blocks in the Predictability of the Final Network. *Supramol. Chem.* **2020**, *32*, 267–275. [CrossRef]
12. Aragoni, M.C.; Arca, M.; Caltagirone, C.; Castellano, C.; Demartin, F.; Garau, A.; Isaia, F.; Lippolis, V.; Montis, R.; Pintus, A. Cationic and Anionic 1D Chains Based on NH+· · · N Charge-Assisted Hydrogen Bonds in Bipyridyl Derivatives and Polyiodides. *CrystEngComm* **2012**, *14*, 5809–5823. [CrossRef]
13. Peloquin, A.J.; McMillen, C.D.; Pennington, W.T. Isolation of Unique Heterocycles Formed from Pyridine-Thiocarboxamides as Diiodine, Iodide, or Polyiodide Salts. *CrystEngComm* **2022**, *24*, 6251–6261. [CrossRef]
14. Wang, H.; Jin, W.J. Cocrystal Assembled by 1,4-Diiodotetrafluorobenzene and Phenothiazine Based on C - I...π/N/S Halogen Bond and Other Assisting Interactions. *Acta Cryst. B* **2017**, *73*, 210–216. [CrossRef] [PubMed]
15. Desijaru, 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*, 1711–1713. [CrossRef]
16. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* **2016**, *116*, 2478–2601. [CrossRef] [PubMed]
17. Aragoni, M.C.; Podda, E.; Chaudhary, S.; Bhasin, A.K.K.; Bhasin, K.K.; Coles, S.J.; Orton, J.B.; Isaia, F.; Lippolis, V.; Pintus, A.; et al. An Experimental and Theoretical Insight into I2/Br2 Oxidation of Bis(Pyridin-2-Yl)Diselane and Ditellane. *Chem. Asian J.* **2023**, *18*, e202300836. [CrossRef]
18. Aragoni, M.C.; Podda, E.; Arca, M.; Pintus, A.; Lippolis, V.; Caltagirone, C.; Bartz, R.H.; Lenardão, E.J.; Perin, G.; Schumacher, R.F.; et al. An Unprecedented Non-Classical Polyinterhalogen Anion Made of $[I_2Cl]^-$ and I_2 at the 2-(*p*-Tolyl)Selenopheno[2,3-*b*]Pyridinium Cation Template. *New J. Chem.* **2022**, *46*, 21921–21929. [CrossRef]
19. Yeo, C.I.; Tan, Y.S.; Kwong, H.C.; Lee, V.S.; Tiekink, E.R.T. I· · · N halogen bonding in 1: 1 co-crystals formed between 1,4-diiodotetrafluorobenzene and the isomeric n-pyridinealdazines (n = 2, 3 and 4): Assessment of supramolecular association and influence upon solid-state photoluminescence properties. *CrystEngComm* **2022**, *24*, 7579–7591. [CrossRef]
20. Pigger, F.C.; Kapadia, P.P.; Swenson, D.C. Halogen bonded networks from pyridyl-substituted tetraarylethylenes and diiodotetrafluorobenzenes. *CrystEngComm* **2013**, *15*, 4386–4391. [CrossRef]
21. Guardigli, C.; Liantonio, R.; Mele, M.L.; Metrangolo, P.; Resnati, G.; Pilati, T. Design and Synthesis of New Tectons for Halogen Bonding-driven Crystal Engineering. *Supramol. Chem.* **2003**, *15*, 177. [CrossRef]
22. Vartanian, M.; Lucassen, A.C.B.; Shimon, L.J.W.; van der Boom, M.E. Cocrystallization of a Tripyridyl Donor with Perfluorinated Iodobenzene Derivatives: Formation of Different N· · · I Halogen Bonds Determining Network vs Plain Packing Crystals. *Cryst. Growth Des.* **2008**, *8*, 786. [CrossRef]
23. Thalladi, V.R.; Weiss, H.C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G.R. C−H· · · F Interactions in the Crystal Structures of Some Fluorobenzenes. *J. Am. Chem. Soc.* **1998**, *120*, 8702–8710. [CrossRef]
24. Rigaku Oxford Diffraction. CrysAlisPro. Software System Version 1.171.39.8d; Rigaku Corporation, Oxford, UK, 2015.
25. Sheldrick, G.M. SHELXT—Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst. A* **2015**, *71*, 3–8. [CrossRef]
26. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3–8. [CrossRef] [PubMed]
27. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [CrossRef]