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Chalcogen-Bonded Cocrystals of Substituted Pyridine *N*-Oxides and Chalcogenodiazoles: An X-ray Diffraction and Solid-State NMR Investigation

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Cite This: http	s://dx.doi.org/10.1021/acs.cgd.0c0	1173 Read Online	-			
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ABSTRACT: We introduce methyl, methoxy, and phenyl sub- stituents at the <i>para-</i> , <i>meta-</i> , and <i>ortho-</i> positions of pyridine <i>N</i> -oxide						

to investigate the effect of chemical substitution on the resulting nine chalcogen-bonded structures formed upon cocrystallization with 3,4-dicyano-1,2,5-selenodiazole and 3,4-dicyano-1,2,5-telluradiazole. Single-crystal X-ray diffraction studies reveal the presence of double chalcogen bonding interactions in the cocrystals and demonstrate the impact of the substitution on the geometric features of the chalcogen bonds. ⁷⁷Se and ¹²⁵Te solid-state NMR spectroscopy is employed to measure selenium and tellurium chemical shift tensors of the products, and various trends are described. The smallest component of the ⁷⁷Se chemical shift tensor (δ_{33}) provides the strongest



correlation with the chalcogen bond distance. Solution NMR provides qualitative evidence for the persistence of the chalcogen bonds in solution. Finally, ${}^{1}J({}^{77}Se, {}^{14}N)$ coupling constants in 3,4-dicyano-1,2,5-selenodiazole and its chalcogen-bonded cocrystals are measured after accounting for residual dipolar coupling between ${}^{77}Se$ and ${}^{14}N$; however, changes in ${}^{1}J({}^{77}Se, {}^{14}N)$ attributable to chalcogen bonding upon cocrystallization are comparable to the experimental uncertainties. This systematic study of chalcogenbonded cocrystals demonstrates the potential utility of the substitution effect for applications of chalcogen bonds in crystal engineering and demonstrates the value of solid-state NMR in characterizing such systems.

INTRODUCTION

Research into σ -hole interactions continues to receive significant attention. Halogen bonds (XB)¹ have been most studied and have found varied applications.² Recently, the focus has expanded toward σ -hole interactions involving the elements of groups 14, 15, and 16 of the periodic table, which results in tetrel bonds,^{3,4} pnictogen bonds,⁵ and chalcogen bonds.⁶⁻⁸ Chalcogen bonding (ChB), analogous to halogen bonding, has been recently defined by IUPAC⁹ as a "net attractive interaction between an electrophilic region associated with a chalcogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity." The highly directional nature of the ChB and the tunability of its strength, similar to XB, have led to them being applied in supramolecular chemistry,^{10–12} molecular recognition,^{13,14} organocatalysis,^{15–18} and medicinal chemistry,^{19,20} for example.

The valence electronic structure of chalcogen atoms allows for the presence of two regions of depleted electron density and elevated positive electrostatic potential (σ -hole),²¹ giving rise to the formation of double chalcogen bonds. There are a limited number of reported examples of double chalcogen bond systems, likely due to limited focus on this area to date and due to steric crowding when larger nucleophiles are used. Striking examples include a series of self-assembled double chalcogen-bonded arrays,^{22–27} self-assembled tubular structures of cyclic diynes,²⁸ self-assembled two-dimensional networks,²⁹ synthesis and characterization of bonding of 3,4-dicyano-1,2,5-telluradiazole adduct and its cocrystals with pyridine and halides,^{30,31} the formation of double chalcogenbonding interactions in chalcogenazolo-pyridine scaffolds,³² and in situ cryocrystallization of diphenyl selenide and diphenyl telluride.³³ In our previous study, dicyanoselenodiazole and dicyanotelluradiazole derivatives acted as supramolecular synthons and formed double chalcogen bonds with diverse electron donors, such as halide anions and oxygen- and nitrogen-containing heterocycles.³⁴

We have explored previously how the NMR response is affected by chalcogen bonding in selected systems. A series of dicyanoselenodiazole and dicyanotelluradiazole chalcogenbonded cocrystals were characterized by a combination of X-

Received: August 21, 2020 Revised: October 9, 2020



ray diffraction and solid-state NMR by our group.³⁴ The relationships between the electronic environment of the chalcogen bond and the ⁷⁷Se and ¹²⁵Te chemical shift tensors were illuminated through a natural localized molecular orbital density functional theory (DFT) analysis. Furthermore, taking inspiration from several studies involving selenocyanate derivatives conducted by Fourmigué and co-workers,³⁵⁻³⁸ we also demonstrated the strong aptitude of benzylic selenocyanates to function as strong and directional ChB donors and interact with halides and nitrogen-containing Lewis bases.³⁹ We further investigated the cocrystals by multinuclear (⁷⁷Se, ¹³C) NMR in the solid state and in solution, as well as with vibrational spectroscopy.^{39,40} However, the effect of chalcogen bonding on the chemical shift was not found to be dominant due to structural diversity in the chalcogen-bonded systems, e.g., monodentate vs bidentate vs tridentate, halide ions vs neutral acceptors, and self-interaction vs intermolecular interaction.

Here, we report a series of cocrystals featuring Ch-···O⁻-N⁺ chalcogen bonds where the chalcogen atoms act as bidentate ChB donors due to the presence of two σ -holes, and the polar but neutral O⁻-N⁺ groups in substituted pyridine N-oxides (PNO) act as bidentate ChB acceptors. 3,4-Dicvano-1,2,5selenodiazole (1) and 3,4-dicyano-1,2,5-telluradiazole (2) are used as ChB donors. Haberhauer and Gleiter have very recently discussed the nature of strong chalcogen bonds to chalcogen-containing heterocycles.⁴¹ Aromatic heterocyclic compounds, such as pyridine derivatives and pyridine Noxide, have been used as electron donors in the case of halogen bonds involving N-haloimides and N-halosaccharins,⁴ bromoresorcinarene derivatives,⁴⁴ 1,*w*-diiodoperfluoroalkane,⁴⁵ tetraiodoethylene,⁴⁶ and perfluorinated aromatics.^{47,48} Different hybridization states of the oxygen atom of the N⁺-O⁻ group result from the electron-donating and electron-withdrawing substituents on the aromatic ring, allowing substituted PNO derivatives to serve as building blocks in supramolecular chemistry.⁴⁹ In the present study, nine new cocrystals involving methyl, methoxy, and phenyl substituents at ortho-, meta-, and para- positions in PNOs (see Scheme 1) have been synthesized and characterized by a combination of singlecrystal X-ray diffraction and solid-state NMR spectroscopy. The substitution at different positions gives rise to distinct geometric arrangements in the various cocrystals, contributing to the observed ⁷⁷Se and ¹²⁵Te chemical shift tensors. This systematic study demonstrates the effect of substitution on the cocrystal structure and provides the potential for crystal engineering applications.

RESULTS AND DISCUSSION

Single-Crystal X-ray Diffraction and Structural Analysis. The dicyanoselenodiazole and dicyanotelluradiazole derivatives 1 and 2 were synthesized according to previous literature.³⁴ The structure of cocrystals of pyridine *N*-oxide itself acting as a ChB acceptor has been previously reported by our group.³⁴ Here, crystals suitable for X-ray diffraction were obtained from slow evaporation at room temperature from a chloroform-acetone solution containing an equimolar ratio of 1 or 2 and PNO derivatives a–f. The structures are shown in Figures 1 and 2. Cocrystallization details and crystallographic data are provided in Tables S1 and S2. The cocrystals are grouped and discussed below based on structural similarities in their crystal packing. The standard ChB parameters, including Ch…X bond distance $(d_{Ch…X})$, N–Ch…X bond angles Article



^aChalcogen bond donors: 3,4-dicyano-1,2,5-selenodiazole (1) and 3,4-dicyano-1,2,5-telluradiazole (2). Chalcogen bond acceptors: 4-methylpyridine *N*-oxide (a), 4-methoxypyridine *N*-oxide (b), 4-phenylpyridine *N*-oxide (c), 3,5-dimethylpyridine *N*-oxide (d), 2,6-dimethylpyridine *N*-oxide (e), and 1,3,5-trimethylpyridine *N*-oxide (f).

 $(\theta_{\text{N-Ch}\cdots X})$, and X···Ch···X bifurcated bond angles $(\theta_{\text{X}\cdots \text{Ch}\cdots X})$, are summarized in Table 1. The ChB distance is also quantified by the normalized contact parameter (N_c) , which is defined as the ratio of the ChB distance between the donor and acceptor atoms to the sum of their van der Waals radii.

Selenium Systems. The X-ray structures reveal a 1:1 ratio of PNO derivative to ChB donor in the asymmetric units of ChB cocrystals of 1.a to 1.d, which crystallized in monoclinic systems with $P2_1/n$ space group in **1**·a, C2/c space group in **1**·c and 1.d, and a triclinic system with $P\overline{1}$ space group in 1.b. These cocrystals feature a similar assembly, where the selenium atom acts as a bidentate ChB donor and interacts with two oxygen atoms from two PNO derivatives, leaving a supramolecular tetrameric ChB synthon with a bifurcated bond angle $\theta_{O\dots Se\dots O}$ of nearly 90°. This geometric feature is similar to the previously reported ChB structure of the cocrystal of dicyanoselenodiazole and PNO.³⁴ The ChB distances range from 2.601(5) Å to 3.126(5) Å with normalized contact values ranging from $N_{\rm C}$ = 0.78 to 0.94. The N–Se…O angles are highly linear, with values ranging from $172.6(1)^{\circ}$ to $178.7(2)^{\circ}$. In cocrystals 1.a, 1.b, and 1.c, pairs of dicyanoselenodiazole molecules are related to each other by an inversion center. The two similar ChB distances in cocrystal 1.c are due to the presence of a glide plane nearly in the center of the oxygen atom and aligned with the long axis of 4-phenylpyridine Noxide. For compounds 1.a, 1.b, and 1.c, there are hydrogen bonds formed between two nitrogen atoms in dicyanoselenodiazole and aromatic hydrogens in ChB acceptors (orange dashed lines), which can stabilize the two ChB interactions. However, in compound 1.d, only one HB interaction is observed between dicyanoselenodiazole and d to stabilize the ChB interaction, leaving one shorter Se…O distance than the other one without HB stabilization (2.601 Å vs 3.126 Å). Furthermore, the formation of HB between the nitrile nitrogen atom and the aromatic hydrogen in the ChB acceptor (except for 1.d where the nitrile nitrogen atom forms HB to its methyl group in ChB acceptor) extends the ChB assembly to twodimensional sheets. Figures depicting these two-dimensional



Figure 1. Chalcogen bond geometry in cocrystals of 3,4-dicyano-1,2,5-selenodiazole with 4-methylpyridine *N*-oxide (1•a), 4-methoxypyridine *N*-oxide (1•b), 4-phenylpyridine *N*-oxide (1•c), 3,5-dimethylpyridine *N*-oxide (1•d), 2,6-dimethylpyridine *N*-oxide (1•e(I), and 1·e(II)), and 1,3,5-trimethylpyridine *N*-oxide (1•f) obtained from single-crystal X-ray diffraction. The HB is shown by an orange dashed line, and the ChB is shown by a black dashed line.



Figure 2. Open spiral configuration in cocrystals of 3,4-dicyano-1,2,5-telluradiazole with 4-methoxypyridine *N*-oxide $(2 \cdot b)$ and 4-phenylpyridine *N*-oxide $(2 \cdot c)$ obtained from single-crystal X-ray diffraction. Shown in the inset is a magnification of the chalcogen bond geometry. The HB is shown by the orange dashed line, and the ChB is depicted by the black dashed line.

sheets are shown in the SI. In 1.b and 1.d, the sheets are parallel to each other, whereas, in 1.a and 1.c, the sheets cross.

Cocrystals **1**•e and **1**•f exhibit different structural features. The asymmetric units of these cocrystals all have 1:1 donor:acceptor ratios. The slow evaporation of a solution containing an equimolar ratio of compound **1** and **e** in chloroform produced cocrystal **1**•e(**I**), which is acicular and crystallizes in a monoclinic system $(P2_1/n \text{ space group})$. This cocrystal has a melting point of 32 °C and easily decomposed at room temperature, which occurred before further analyses could be completed. The formation of only a single ChB between dicyanoselenodiazole and 2,6-dimethylpyridine *N*-oxide, shown at the bottom in Figure 1, could be due to the steric constraints imposed by the substituents on the PNO molecules. Instead, another ChB interaction takes place between the selenium atom and the nitrogen atom of the

nitrile group from the next dicyanoselenodiazole molecule. This Se---N interaction leads to the formation of a onedimensional polymeric chain aligned with the crystallographic *c* axis in $1 \cdot e(I)$. The Se…O distance was measured to be 2.650(2) Å with an N_c value of 0.80, and the Se…N distance was measured to be 3.222(3) Å with an N_c value of 0.93. The instability of $1 \cdot e(I)$ makes it challenging to be reproduced. Cosublimation⁵¹ was used to try to re-prepare this polymorph; however, this method generated a second polymorph of cocrystal 1.e, labeled as 1.e(II). This more thermally stable polymorph was amenable to solid-state NMR and PXRD analyses. This polymorph crystallizes in a brick-shaped monoclinic system (C2/c space group). Instead of a chainlike geometry, a discrete ChB assembly is formed with two donors and two acceptor molecules, in which the two dicyanoselenodiazole molecules are related by an inversion

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Гable 1. Summary of Local Chalcogen Bondi	g Geometrical Information from	Single-Crystal X-ray Diffraction
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	Х	$d_{\mathrm{Ch}\cdots\mathrm{X}}/\mathrm{\AA}$	$N_{\rm c}^{\ a}$	$\theta_{\text{N-Ch}\cdots\text{X}}/^{\circ}$	$ heta_{\mathrm{X}\cdots\mathrm{C}\mathrm{h}\cdots\mathrm{X}}/^{\circ}$	
1·PNO	0	2.786(2)	0.84	179.01(8)	89.95(6)	ref 34
		2.773(2)	0.84	174.78(8)		
1•a	0	2.757(3)	0.83	175.5(1)	94.4(1)	this work
		2.796(3)	0.84	173.7 (1)		
1•b	0	2.784(2)	0.84	176.34(9)	93.64(6)	this work
		2.704(2)	0.81	173.82(9)		
1•c	0	2.756(3)	0.83	174.8(1)	86.13(7)	this work
		2.758(2)	0.83	172.6(1)		
1•d	0	2.601(5)	0.78	178.7(2)	95.2(1)	this work
		3.126(5)	0.94	175.4(2)		
1•e(I)	0	2.650(2)	0.80	165.90(7)	98.98(5)	this work
	Ν	3.222(3)	0.93	171.19(7)		
1•e(II)	0	2.614(2)	0.79	171.09(5)	117.08(4)	this work
	Ν	3.097(2)	0.89	163.86(6)		
1•f	0	2.654(5)	0.80	165.8(2)	94.7(1)	this work
	Ν	3.199(6)	0.92	178.9(2)		
2·PNO	0	2.655(5)	0.76	161.93(2)	121.7	ref 34
		2.633(5)	0.75	160.02(2)		
2 · b	0	2.573(2)	0.74	167.88(7)	103.76(5)	this work
		2.767(2)	0.79	172.62(8)		
2•c	0	2.627(3)	0.75	167.8(1)	103.23(8)	this work
		2.757(3)	0.79	173.2(1)		
				. ,		

^{*a*}Normalized contact parameter: $N_c = \frac{d_{Ch...X}}{\Sigma d_{vdW}}$. The van der Waals radii of the corresponding atoms used in the calculation are obtained from previous literature with values of 1.66 Å for nitrogen, 1.50 Å for oxygen, 1.82 Å for selenium, and 1.99 Å for tellurium.⁵⁰



Figure 3. An example of a comparison of the experimental PXRD pattern of cocrystal 1·a (top, black) and the simulated pattern obtained from the single-crystal structure (bottom, red).

center. In addition to the Se-O ChB interaction with 2,6dimethylpyridine N-oxide ($d_{\text{Se}\cdots\text{O}} = 2.614$ Å and $N_{\text{c}} = 0.79$), there is also formation of a Se…N ChB dimer with its neighboring diazole moiety ($d_{\text{Se}\cdots\text{N}} = 3.097$ Å and $N_{\text{c}} = 0.89$). Similar to cocrystal 1·e(I), compound 1·f also features a similar chain-like Se…N interaction between the selenium atom and the nitrile nitrogen atom of the second dicyanoselenodiazole molecule along the crystallographic a axis. The Se-O distance was measured to be 2.654(5) Å with an N_c value of 0.80, and the Se…N distance was measured to be 3.199(6) Å with an N_c value of 0.92. We observe that there is a shorter ChB distance (smaller $N_{\rm c}$ values) between selenium and oxygen atoms compared to the distance between selenium and nitrogen atoms in these three cocrystals, most probably attributable to the electron-rich environment present in the dipolar O⁻-N⁺ motif in PNOs. However, there is less linearity of the ChB interaction when oxygen acts as a ChB acceptor compared to the nitrogen atom.

Tellurium Systems. ChBs present in the tellurium systems display a different structural geometry. Both tellurium donors and oxygen acceptors are bidentate; however, instead of forming a closed tetrameric synthon, they form an intriguing open spiral shape around a 2-fold screw axis aligned with the crystallographic *b* axis in cocrystal **2**•**b** and *c* axis in cocrystal **2**•**c** (Figure 2). This is different from the discrete ChB assembly previously observed in the cocrystal of dicyanotelluradiazole and unsubstituted PNO.³⁴ Two HB interactions between the heterocyclic nitrogen in the ChB donor and aromatic hydrogen in the ChB acceptor further stabilized the Te···O ChB interaction in compound **2**•**c**, resulting in ChB distances of 2.627(3) and 2.757(3) Å with nearly linear ChB angles of 167.8(1)° and 173.2(1)°. However, only one hydrogen bond is

noted between the heterocyclic nitrogen atom and aromatic hydrogen atom in 2.b, leading to a shorter ChB distance of 2.573(2) Å with HB stabilization and a longer ChB distance of 2.767(2) Å without HB stabilization.

These results show that the selenium atom in dicyanoselenodiazole acts as a bidentate ChB donor and interacts with para-/meta-substituted PNOs, resulting in a supramolecular tetrameric ChB synthon with moderate shorter and directional ChB interactions; however, this geometrical feature can be disrupted by the steric hindrance present in ortho-substituted PNOs. In dicyanotelluradiazole, the tellurium atom also acts as a bidentate ChB donor with para-substituted PNOs, resulting in an open spiral configuration. With the same ChB acceptors, we observe that there are smaller N_c values in the tellurium system compared to the selenium system due to the higher polarizability and more positive σ -hole present in the tellurium atom. It has been shown by ΔE_{int} calculations that the addition of electron-donating groups increases the strength of XB, and that the XB between tetraiodoethylene and phenyl-substituted PNOs is stronger than the one with methyl-substituted PNOs.⁴⁶ In our study, the average ChB distances were found to follow the following trend: methoxy-substituted PNO < phenyl-substituted PNO < methyl-substituted PNO < PNO, when the substituents are at the same position. It is important to remember that the ChB distances do not necessarily represent the strength of ChB or ΔE_{int} (see in SI) since other interactions, such as HB in this case, can contribute to the stabilization of the complexes.

Powder X-ray Diffraction. Sample phase purity was verified by comparing the experimental X-ray powder diffractograms to those simulated based on the experimental single-crystal X-ray structures (see SI). One example of a comparison between the experimental X-ray powder diffractograms of cocrystal 1.a and its simulated pattern based on the single-crystal X-ray structure is provided in Figure 3. Compared to the simulated PXRD pattern, cocrystal 1.f has a slightly different experimental PXRD result, shown in Figure S5. The presence of some peaks that do not align with the peaks representing the starting material, and some slightly shifted peak positions, indicate an inconsistency between the polycrystalline sample and the single-crystal structure. This inconsistency could be attributable to the different temperatures in the data collection (200 K for single-crystal X-ray diffraction vs room temperature for PXRD). In addition, the effect of heat and pressure generated during the mechanical grinding may also cause the difference in the simulated and experimental patterns.^{52,53}

NMR Spectroscopy. Chemical Shift Tensors. Selenium and tellurium are spin- $^{1/}{_2}$ nuclei with moderate natural abundances (7.58% for ^{77}Se and 6.99% for $^{125}Te)$ and gyromagnetic ratios ($\gamma = 5.12 \times 10^7$ rad T⁻¹ s⁻¹ for ⁷⁷Se and $\gamma = -8.498 \times 10^7$ rad T⁻¹ s⁻¹ for ¹²⁵Te). Their broad chemical shift ranges of approximately 3000 ppm for ⁷⁷Se^{54,55} and 6000 ppm for ¹²⁵Te^{55,57} suggest that they can be highly sensitive probes of their local environments. Our group has directly probed the ChB interaction in cocrystals involving seleno and telluradiazole derivatives³⁴ and benzylic selenocyanates⁴⁰ by ⁷⁷Se and ¹²⁵Te solid-state NMR; however, correlations between local structural features and the chemical shift tensors are not always clear due to the diversity of packing arrangements present in the cocrystals.

The ⁷⁷Se and ¹²⁵Te cross-polarization magic-angle spinning (CP/MAS) NMR spectra of the polycrystalline ChB cocrystals studied in this work are shown in Figures 4 and 5. Spectra were



Figure 4. Experimental ⁷⁷Se CP/MAS SSNMR spectra (black) obtained at 9.4 T for cocrystals: 1.a (a), 1.b (b), 1.c (c), 1.d (d), 1.e (II) (e), and 1 f (f). The corresponding simulated spectra are shown at the top (red). Asterisks indicate the isotropic peaks. The spectra were acquired at a spinning speed of 3 kHz.



Figure 5. Experimental ¹²⁵Te CP/MAS SSNMR spectra (black) obtained at 9.4 T for cocrystals $2 \cdot b$ (a) and $2 \cdot c$ (b). The corresponding simulated spectra are shown at the top (red). The isotropic peaks are indicated by asterisks. The spectra were acquired at a spinning speed of 6 kHz.

acquired at two different MAS frequencies to differentiate the isotropic peaks from the spinning sidebands. The CS tensor parameters (isotropic chemical shift (δ_{iso}) , span (Ω) , and skew (κ)) obtained from a Herzfeld–Berger analysis are reported in Table 2.

There are two crystallographically distinct selenium sites observed in starting material 1. DFT calculations help to assign the two peaks, in which the larger chemical shift (1591.8(0.1))ppm) corresponds to the selenium site involved in three ChB interactions and the smaller chemical shift value (1547.9(0.1))ppm) corresponds to the selenium site with two ChB interactions.³

For all the chalcogen-bonded cocrystals, the intermediate and most shielded principal components of the ⁷⁷Se chemical shift tensor (δ_{22} and δ_{33}) are observed to increase, ranging from 1490(2) ppm to 1649(5) ppm and 1359(3) ppm to

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Table 2. Experimental ⁷⁷Se and ¹²⁵Te Chemical Shift Tensor Components and $J(^{77}Se, {}^{14}N)$ Values for 1 and 2 and All the Cocrystals under Investigation

	$\delta_{ m iso}/ m ppm$	Ω/ppm	κ	$\delta_{11}/{ m ppm}$	$\delta_{22}/{ m ppm}$	$\delta_{33}/{ m ppm}$	J(⁷⁷ Se, ¹⁴ N) /Hz
1	1547.9(0.1)	482(5)	-0.44(0.04)	1824(7)	1477(7)	1342(1)	78(4)
	1591.8(0.1)	488(4)	0.04(0.01)	1833(2)	1598(4)	1345(3)	79(4)
1.PNO ^a	1563.7(0.1)	375(2)	-0.08(0.01)	1756(2)	1554(1)	1381(1)	
1•a	1610.0(0.1)	442(2)	0.14(0.01)	1821(3)	1631(2)	1379(2)	76(4)
1•b	1608.7(0.1)	452(10)	0.27(0.03)	1815(5)	1649(5)	1363(5)	76(4)
1•c	1567.7(0.1)	421(3)	-0.03(0.01)	1780(4)	1563(3)	1359(3)	74(4)
1∙d	1579.9(0.1)	400(4)	-0.21(0.02)	1794(4)	1552(3)	1394(3)	80(20)
1•e(II)	1554.0(0.1)	401(2)	-0.48(0.01)	1787(3)	1490(2)	1386(2)	b
1•f	1574.2(0.1)	459(5)	-0.44(0.02)	1837(4)	1507(2)	1378(3)	b
2 ^{<i>a</i>}	2332.8(0.1)	1268(3)	0.49(0.01)	2863(5)	2540(3)	1595(4)	b
2·PNO ^a	2420.1(0.1)	822(4)	0.42(0.02)	2774(8)	2535(5)	1952(5)	b
2·b	2402.3(0.1)	980(13)	0.50(0.01)	2811(4)	2566(2)	1831(9)	b
2•c	2444.9(0.1)	1024(28)	0.40(0.02)	2888(11)	2582(4)	1864(17)	ь

^aValues were taken from ref 34. ^bValues were not measured.



Figure 6. Plots of δ_{33} (⁷⁷Se) as a function of ChB distance $d_{Ch\cdots X}$ (a) and normalized distance parameter N_c (b). Data points corresponding to compounds 1·PNO, 1·a, 1·b, 1·c, 1·d, and 1·e(II) are shown in blue, and data points corresponding to compound 1·f are shown in orange (see text for discussion of these outliers). The solid black line corresponds to a linear fit, and a dashed red line corresponds to an exponential fit.

1394(3) ppm, respectively, compared to a δ_{22} value of 1477(7) ppm and a δ_{33} value of 1342(1) ppm in pure compound 1. Here, we only compare to the values for the selenium site with two ChB interactions in 1 since the selenium atom in the cocrystals acts as a bidentate ChB donor, which only interacts with two acceptor atoms. The most deshielded component, δ_{11} , generally decreases in the cocrystals (1·a, 1·b, 1·c, and 1·d) with similar geometry and 1.e, varying from 1756(2) ppm to 1821(3) ppm, but increases in the cocrystal 1.f (1837(4) ppm), relative to pure 1. The combined changes in the three principal components lead to an increasing isotropic chemical shift, which is the average of the three principal components, and a decreasing span value, which is the difference between δ_{11} and δ_{33} values, upon cocrystallization. These observations are consistent with most cases reported in the literature.^{34,40} In addition, in the cocrystals where a supramolecular tetrameric ChB synthon is formed, non-axially symmetric chemical shift tensors (κ values are close to zero) tend to be observed. This is particularly evident for 1.PNO and 1.c, where the two ChB interactions are very similar to $\Delta d_{\text{Ch} \cdots \text{X}}$ (difference in two $d_{\text{Ch} \cdots \text{X}}$ within the system) of ~0.013 Å and ΔN_c (difference in two N_c within the system) of ~0.04: the κ values are very close to zero (-0.08(0.01) and -0.03(0.01), respectively) compared to a κ of -0.44 in pure compound 1.

Similar observations are noted in the tellurium systems: δ_{22} and δ_{33} of the ¹²⁵Te chemical shift tensor increase in ChB cocrystals **2·b** and **2·c** compared to starting material **2**, for which $\delta_{22} = 2540(3)$ ppm and $\delta_{33} = 1595(4)$ ppm. The value

of δ_{iso} increases in the chalcogen-bonded cocrystals, ranging from 2402.3(0.1) ppm to 2444.9(0.1) ppm, compared to δ_{iso} of 2332.8(0.1) ppm in **2**. The span of the ¹²⁵Te chemical shift tensor (Ω) is smaller in the chalcogen-bonded cocrystals (ranging from 822(4) ppm to 1024(28) ppm) than in pure **2** (1268(3) ppm).

Periodic DFT calculations of ⁷⁷Se magnetic shielding tensors were performed on all the compounds in this study. The computational details and a comparison between the experimental and calculated isotropic chemical shifts are provided in the SI. There is only a weak correlation between the experimental and computed results. The reasons for this weak correlation are unclear, given that the crystal lattice is included using periodic boundary conditions and that relativistic effects are included using the zeroth-order regular approximation.

It has been reported that, in most cases of σ -hole interactions, a more linear interaction (bond angle is close to 180°) and shorter bond distance (smaller $d_{Ch\cdots X}$ values and smaller N_c values) correspond to a stronger interaction. Here, we plotted all the experimental chemical shift tensor data for the cocrystals (δ_{iso} , Ω , κ and δ_{11} , δ_{22} , δ_{33} components) as a function of the typical geometrical parameters associated with ChB ($d_{Ch\cdots X}$, N_c , and $\theta_{N-Ch\cdots X}$); see the SI. Since the selenium is a bifurcated donor, we use the average values of these structural parameters. Only the most shielded principal components, δ_{33} , show any correlation to $d_{Ch\cdots X}$ and N_c parameters, but even these are weak, as seen in Figure 6.

The data point corresponding to 1·f (shown in orange) is scattered from the primary trend, which may result from the inconsistency between the experimental and simulated PXRD patterns as mentioned above. Generally, however, the δ_{33} values decrease as the ChB distance shortens, following a weak linear correlation ($R^2 = 0.7664$). The plot of δ_{33} versus N_c provides a slightly different trend as shown in Figure 6b. The correlation is stronger when fit with a polynomial ($R^2 = 0.8779$) rather than a linear function ($R^2 = 0.6970$). While this correlation is consistent with the theoretical trend previously observed for the model of dicyanoselenodiazole and tetrabutylammonium halides,³⁴ the physical meaning of the polynomial fit is unclear. The nonlinear trend could also result from the N···H HB that stabilizes the ChB interaction.

J Coupling between ⁷⁷Se and ¹⁴N. As shown in Figure 7, we noted that the isotropic ⁷⁷Se peak for site 1 of compound 1



Figure 7. Experimental isotropic ⁷⁷Se peaks obtained from CP/MAS SSNMR spectra at 9.4 T with a spinning speed of 10 kHz for site 1 of the starting material **1**. The corresponding simulated spectra are shown at the top (red). Shown in the inset (right) are the experimental and simulated ⁷⁷Se NMR spectra acquired at 11.7 T.

exhibits a quintet-like fine structure. Additional ⁷⁷Se CP/MAS SSNMR data were also acquired at 11.7 T, shown in the inset, to prove that this fine structure is due to coupling between ⁷⁷Se and two covalently bonded ¹⁴N instead of resulting from an impurity or from crystallographically distinct sites. The coupling between ⁷⁷Se and two covalently bonded ¹⁴N can also be observed in the spectra of compounds 1.a, 1.b, 1.c, and 1.d (see Figure S16). The effect of quadrupolar ¹⁴N (spin I =1) coupling to ⁷⁷Se results in multiplets that are squeezed or expanded relative to the middle peak (77 Hz splitting at the high frequency side vs 85 Hz splitting at the low frequency side in Figure 7). Thus the observed splittings are not exactly equal to the value of $|J(^{77}Se, {}^{14}N)|$; rather, residual dipolar coupling must be considered and accounted for using spectral simulations.⁵⁸ Two covalent bond distances between the selenium and nitrogen atoms were approximated as equal (the difference is shorter than 0.006 Å based on the diffraction structure). Therefore, the experimentally observed splitting was modeled as a triplet of asymmetric triplets⁵⁹ with the same $|J(^{77}Se, ^{14}N)|$ for each ^{14}N site, and the simulations were generated by adding two sites separately, in which the magnitude of one J value is set to be double of the other one. The simulations were generated using WSolids software,⁶ shown in red, and depend on the direct dipolar coupling (R_{DD}) and *J* coupling between ⁷⁷Se and ¹⁴N, the quadrupolar coupling constant of ¹⁴N (C_0), and the angle between the largest

principal component of the electric field gradient tensor (V_{33}) and the Se-N bond (β) . The R_{DD} value, $R_{\rm DD} = \frac{\gamma_{\rm sc}\gamma_{\rm N}\mu_0}{4\pi} \frac{\hbar}{2\pi} \langle r_{\rm Se-N}^{-3} \rangle$, which depends on the inverse cube of the motionally averaged internuclear distance, can be calculated directly from the single-crystal X-ray structure. The quadrupolar asymmetry parameter $\eta_{\rm O}$ did not noticeably affect the simulation, and hence was set to be zero. The only adjusted parameters during the fitting process were therefore C_0 , β , and J(⁷⁷Se, ¹⁴N)l; all values used in the simulations are summarized in the SI and the J coupling data are also provided in Table 2. This analysis excludes potential effects from ¹⁴N-¹⁴N dipolar coupling between two ¹⁴N atoms in the same molecule. This is a reasonable assumption given that these dipolar couplings are only ~36 Hz based on the X-ray structures. The analysis also assumes the coupling from ¹⁴N in the PNO moieties (\sim 30 Hz) is negligible.

Given the negligible change in the line width of the isotropic peaks obtained from two magnetic fields, the effect from residual dipolar coupling is small⁶¹ (*viz*. $|C_Q|^{(14}N)| < 5$ MHz). The magnitude of $C_Q(^{14}N)$ is consistent with DFT calculations (see in Table S4). The $|J|^{(77}Se, ^{14}N)|$ values of starting material 1 are estimated to be 78(4) Hz for site 1 and 79(4) Hz for site 2 (Table 2). The $|J|^{(77}Se, ^{14}N)|$ values for the cocrystals range from 74(4) Hz for compound 1·c to 80(20) Hz for compound 1·d. The magnitude of these $|J|^{(77}Se, ^{14}N)|$ values is reproduced by DFT calculated values of ~100 Hz, provided in Table S4. There is a slight decrease in $|J|^{(77}Se, ^{14}N)|$ in the cocrystals compared to the starting material, except for compound 1·d, in both experimental and calculated results. However, the poor resolution and line broadening observed experimentally result in relatively significant errors; therefore, we are unable to draw clear conclusions regarding any trends in *J* coupling with respect to ChB geometry or strength.

Solution NMR. ⁷⁷Se and ¹²⁵Te solution NMR spectroscopy is also highly sensitive to changes in the electronic and structural environment of chalcogen bonds.^{11,62} Also of note, Rissanen and co-workers recently used ¹H, ¹⁵N-HMBC studies to measure the ¹⁵N chemical shift of pyridine N-oxides and their XB complexes and used the chemical shift changes as a qualitative assessment of the strength of N-I···⁻O-N⁺ and N-Br···⁻O-N⁺ XB interactions indirectly. Here, we used ⁷⁷Se and ¹²⁵Te chemical shift changes ($\Delta \delta = \delta$ (ChB cocrystals) – δ (starting material)) to directly investigate the strength of Se…⁻O-N⁺ chalcogen bonding in solution. As summarized in Table S3 (SI), ChB formation between compound 1 and most pyridine N-oxide derivatives in CDCl₂ leads to deshielding in the ⁷⁷Se NMR spectrum, ranging from +2.19 ppm for 1·a to +14.06 ppm for 1.c, relative to that for pure selenodiazole, except for cocrystals 1·e ($\Delta\delta$ = -0.78 ppm) and 1·f ($\Delta\delta$ = -1.86 ppm). The chemical shift change follows the following trend: $\Delta\delta(1\cdot \mathbf{c}) > \Delta\delta(1\cdot \mathbf{PNO})^{34} > \Delta\delta(1\cdot \mathbf{b}) > \Delta\delta(1\cdot \mathbf{d}) >$ $\Delta\delta(1\cdot a)$, thus representing the effect of substituents: $\Delta\delta$ - $(\text{phenyl-PNO}) > \Delta\delta(\text{PNO}) > \Delta\delta(\text{methoxy-PNO}) > \Delta\delta$ (methyl-PNO). This trend parallels what has been observed for XB association constants between N-iodosaccharin and pyridine N-oxides determined by ¹H NMR in CDCl₃, where K_{XB} (phenyl-PNO) > K_{XB} (PNO) > K_{XB} (methyl-PNO) > K_{XB} (methoxy-PNO).⁴³ The small values found for methoxy-PNO were rationalized by the competitive interference from the water in the NMR solvent and the use of the hydrated form of methoxy-PNO.43 Unexpected chemical shift changes observed for cocrystals 1.e and 1.f may be attributed to (1)

water content in the NMR solvent can compete with selenium and form HB with PNO; (2) steric hindrance from PNO allows the selenium to have only one ChB instead of acting as bifurcated ChB donor.

Compound **2** and its ChB cocrystals were dissolved in DMSO- d_6 due to the reduced solubility of all telluriumcontaining samples in CDCl₃. However, there is no consistent increase or decrease in the chemical shifts of the cocrystals observed compared to the value of pure telluradiazole **2** (δ = 2430.02 ppm). This inconsistency is attributed to the solvent effect, where the oxygen atom in DMSO can also act as a ChB acceptor and compete with the oxygen atom in the pyridine *N*oxides.

CONCLUSIONS

Nine new chalcogen-bonded cocrystals involving dicyanoselenodiazole/dicyanotelluradiazole and pyridine N-oxide derivatives have been synthesized and characterized through a combination of X-ray diffraction and NMR spectroscopy. The geometric information demonstrates that these ChB are moderately short and directional. Without steric hindrance, cocrystals formed between dicyanoselenodiazole and pyridine N-oxides featured a supramolecular tetrameric ChB synthon, and cocrystals formed between dicyanotelluradiazole and pyridine N-oxide derivatives exhibit an open spiral configuration. Different substituents at the para- position of pyridine N-oxide result in a ChB distance trend similar to that in previous studies of halogen-bonded systems: methoxysubstituted PNO < phenyl-substituted PNO < methylsubstituted PNO < PNO. However, these ChB distances do not necessarily directly reflect the strength of ChB due to additional hydrogen bonding stabilization of some complexes.

Both ⁷⁷Se and ¹²⁵Te CP/MAS SSNMR experiments reveal a general increase in the δ_{22} and δ_{33} principal components of chemical shift tensors for the chalcogen-bonded cocrystals in comparison to the pure dicyano-1,2,5-seleno/telluradiazoles, resulting in an increase in isotropic chemical shift and a decrease in span values. Fine structure in the ⁷⁷Se solid-state NMR spectra originating from residual dipolar coupling and *J* coupling to ¹⁴N was successfully modeled in order to determine intramolecular $J(^{14}N, ^{77}Se)$ coupling values. Unfortunately, the changes observed upon cocrystallization did not significantly exceed the errors on the data and therefore no definitive trend resulting from chalcogenbonding-induced cocrystallization could be confirmed.

Overall, this work demonstrates that different chemical substitution patterns on chalcogen bond acceptors can give rise to different structural geometries and crystal packing arrangements in the chalcogen-bonded cocrystalline products. These systems are characterized by different NMR responses, thereby contributing to a growing understanding of the impact of σ -hole interactions on NMR interaction tensors.

EXPERIMENTAL SECTION

Synthesis. Starting materials were purchased from Sigma-Aldrich, TCI, or Apollo Scientific. Commercial AR grade solvents were used without further purification for the synthesis of 3,4-dicyano-1,2,5-seleno/telluradiazoles and 2,4,6-trimethyl pyridine *N*-oxide, and for the cocrystallization of chalcogen-bonded products. 3,4-Dicyano-1,2,5-seleno/telluradiazoles were synthesized as previously reported.³⁴ ¹H, ¹³C, and ⁷⁷Se/¹²⁵Te solution NMR experiments were used to confirm the purity of the products.

Synthesis of 2,4,6-trimethylpyridine N-oxide was adapted from the synthesis of 2,6-dimethylpyridine 1-oxide in the literature.⁶³ 2,4,6-Collidine (5 mL, 43 mmol), acetic acid (ca. 25 mL), and hydrogen peroxide (ca. 20 mL) were mixed together and refluxed at 90 °C. After 4 h, additional hydrogen peroxide (ca. 25 mL) was added, and the reaction was left to reflux for 5 days. The reaction was monitored by TLC analysis in 95:5 dichloromethane/methanol. Upon completion, the reaction mixture was reduced to about a third of its volume under reduced pressure and was diluted with an excess of distilled ice water. The pH was then adjusted to ~ 10 by use of K₂CO₃ and confirmed with litmus paper. The crude product was obtained via extraction with CH₂Cl₂. The product was purified through column chromatography by eluting with 1:1 hexane/ethyl acetate, then with 9:1 dichloromethane/methanol. ¹H and ¹³C solution NMR experiments were used to confirm the purity of the product. ¹³C NMR (300 MHz, CDCl₃) δ in ppm: 148.47 (1C), 136.36 (1C), 125.06 (2C), 20.50 (2C), 18.50 (2C). ¹H NMR (300 MHz, CDCl₃) δ in ppm: 6.93 (s, 2H), 2.48 (s, 6H), 2.25 (s, 3H)

Cocrystallization. Equimolar amounts of ChB donor 1 or 2 and ChB acceptors, 4-methylpyridine N-oxide (a), 4-methoxypyridine N-oxide (b), 4-phenylpyridine N-oxide (c), 3,5-dimethylpyridine N-oxide (d), 2,6-dimethylpyridine N-oxide (e), and 2,4,6-trimethylpyridine N-oxide (f), were dissolved into a minimum volume of chloroform for cocrystals involving selenium systems, or acetonitrile or acetone for cocrystals involving tellurium systems. Slow evaporation of these solvents at room temperature produced cocrystals suitable for single-crystal X-ray diffraction. Solids were stored in a refrigerator at ~4 °C. Melting points were determined with a MEL-TEMP electro-thermal instrument.

Cosublimation. 3,4-Dicyano-1,2,5-selenodiazole (1) and 2,6dimethylpyridine *N*-oxide (e) were added separately to opposite ends of a 2.5 mm diameter glass tube. The tube was then sealed in vacuo. In a home-built, two-zone tube furnace,⁵¹ the temperature of each end of the tube was monitored separately, where the zone containing starting material **1** was heated from 20 to 90 °C at a rate of 10 °C/h and the zone containing 2,6-dimethylpyridine *N*-oxide was heated from 20 to 55 °C at a rate of 5 °C/h. Each end of the sublimation tube was held at final temperatures for 10 h and was allowed to slowly return to room temperature over 7 h. The polymorph **1**·e(**II**) was collected near the center of the tube.

Solution NMR Spectroscopy. ⁷⁷Se and ¹²⁵Te NMR spectra were recorded using a 300 MHz Bruker Avance II NMR spectrometer at ambient temperature. The external reference for ⁷⁷Se was selenous acid (1 M solution in D_2O), with a chemical shift of 1300.1 ppm. The external reference for ¹²⁵Te was diphenyl ditelluride (0.5 M solution in CDCl₃) with the chemical shift set to 420 ppm. 0.01 M solutions were prepared in CDCl₃ and DMSO-*d*₆ to acquire ⁷⁷Se and ¹²⁵Te NMR spectra, respectively. Commercial deuterated solvents from Cambridge Isotope Laboratories Inc. were used without further purification.

Solid-State NMR Spectroscopy. Data were acquired with a 9.4 T magnet ($\nu_{\rm L}$ (⁷⁷Se) = 76.31 MHz and $\nu_{\rm L}$ (¹²⁵Te) = 126.24 MHz), Bruker AVANCE III console, and a triple-resonance 4 mm MAS probe (University of Ottawa, Ottawa, Canada). Samples were ground into fine powders and packed into 4 mm o.d. zirconia rotors. ⁷⁷Se chemical shifts were referenced to solid ammonium selenate (δ_{iso} = 1040.2 ppm), and ¹²⁵Te chemical shifts were referenced to solid telluric acid (δ_{iso} = 685.5 and 692.2 ppm). A standard ${}^{1}\text{H} \rightarrow {}^{77}\text{Se}/{}^{125}\text{Te}$ cross-polarization (CP) pulse sequence was employed for all the cocrystals. The $\pi/2$ pulse length was 4.1 μ s for ⁷⁷Se and 3.4 μ s for ¹²⁵Te. The contact time was set to be 7 ms for ⁷⁷Se and 2 ms for ¹²⁵Te. The recycle delay ranged from 10 s to 4 min. The total number of transients ranged from 1184 to 11784. The read-out temperature was held constant at 298 K for most of the experiments, or at 288 K for compounds with a low melting point, using an FTS Systems TC-84 temperature controller. To identify the isotropic peak and to obtain spectra with a larger number of sidebands for spectral fitting purposes, the SSNMR data were acquired with two different MAS frequencies (3 kHz and 10 kHz for $^{77}\text{Se},$ 6 kHz and 11 kHz for $^{125}\text{Te}).$

Additional ${}^{1}\text{H} \rightarrow {}^{77}\text{Se CP/MAS}$ experiments were performed at 11.7 T to identify the presence of field-dependent splittings.

Powder X-ray Diffraction. All PXRD patterns were obtained using a Rigaku Ultima IV powder diffractometer at 298 K (± 2) (CuK α_1 radiation with a wavelength of $\lambda = 1.54056$ Å). The measurements were taken using one diffracted beam monochromator with a step-scan technique from 5° to 50° (2θ range) in increments of 0.02° with a scan rate of 1°/min. Simulations were generated using Mercury 4.2.0 software from the Crystallographic Data Center. Comparisons between experimental PXRD patterns and simulated patterns from the single-crystal structure were used to verify sample phase purity and are provided in the SI.

Single-Crystal X-ray Diffraction. The crystals were mounted on glass fibers or transparent MiTeGen MicroMounts precision tools prior to data collection. The data were collected on a Bruker Kappa Apex and Smart Apex diffractometer equipped with MoK α radiation (wavelength of $\lambda = 0.7103$ Å) with an APEX II CCD detector at 200 \pm 2 K. The raw data collection and processing were performed with the Bruker APEX III software package. Crystal structures of the cocrystals were solved using WinGX and Olex2 software packages with the direct method and refined against F^2 using SHELXL97. Packing diagrams were generated using Mercury 4.1.0 and POV-Ray. Intermolecular interactions were analyzed with PLATON. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using difference Fourier maps or positioned geometrically.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c01173.

Additional powder X-ray diffractograms, crystal packing diagrams, plots of NMR data, further computational details, further experimental details, additional NMR spectra, and additional crystallographic data (PDF)

Accession Codes

CCDC 2016654, 2016655, 2016657, 2016658, 2016660– 2016663, and 2016670 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.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

D.L.B. is grateful to the Natural Sciences and Engineering Research Council of Canada for funding.

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