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ARTICLE

Temperature-dependent halogen...halogen synthon crossover in coordination compounds

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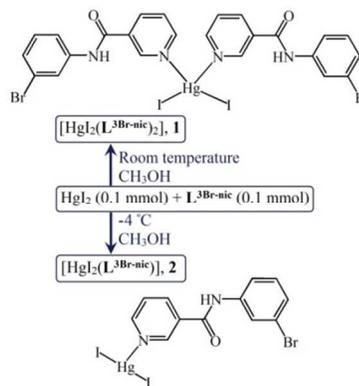
The temperature-dependent Br...Br halogen...halogen synthon crossover in two coordination compounds of HgI₂ and *N*-(3-bromophenyl)pyridine-3-carboxamide flexible ligand, **L**^{3Br-nic}, have been investigated. Results show that when starting with equivalent amount of reagents and when the reaction was carried out at room temperature, a 1:2 adduct of the HgI₂:2**L**^{3Br-nic}, complex **1**, was generated, whereas when the reaction temperature was fixed at -4 °C, a 1:1 adduct, complex **2**, was obtained. In **1**, individual molecules form a wave-like chain through the type II Br...Br halogen bonding interactions, while Br...Br interaction generates dimeric units in **2**.

Introduction

The design of structural assemblies in coordination compounds has received more attention in recent years due to various promising applications.¹ However, rationally controlling the desired structures of crystalline coordination compounds still remains a great challenge.² Due to the high versatility of a self-assembly system, even when starting from the same reagents, the structural uncertainty of the coordination compounds and may result in the formation of complexes with different network structures and different chemical compositions.³ In this regard, the shape and bonding mode of the ligand⁴ and also the preferred coordination geometry of the metal ion,⁵ as the primary considerations, affect the self-assembly process. In addition to these two factors, a number of experimental variables such as the solvent,⁶ reacting time,⁷ reagent ratio,⁸ counter ions,⁹ template effect,¹⁰ temperature,¹¹ and pH¹² can also affect the final structures. Among these temperature is very important in controlling the self-assembly of the structures. Notably, only a few examples of temperature-dependent supramolecular isomers and motifs have been investigated.¹³ Previously, the temperature-dependent structures of 1D and 2D HgCl₂ coordination polymers containing a *N*-(2-pyridylmethyl)-2-pyrazinecarboxamide flexible ligand with different motifs by controlling the reaction temperature have been reported by some of us.¹⁴ Nevertheless, precise control of the final structural architecture by varying temperature is still rare.¹⁵

The influence of intermolecular interactions on the formation of crystal packing of coordination compounds has been well studied. When more than one type of interaction can be formed between motifs, the exploration of how these non-covalent interactions work competitively or cooperatively in the self-assembly process is important.¹⁶ It is notable that when intermolecular interactions are likely to interfere with one other, they can compete. The presence of such competition between different motifs called “synthon crossover”.¹⁷ Recently, synthon crossover between halogen...π and halogen...halogen interaction in a series of *N*-(4-halophenyl)-2-naphthamide and *N*-(4-halophenyl)quinoline-2-carboxamide and

also Br...Br and Br...N in conformational polymorphism have been reported by some of us.¹⁸ To our knowledge, no structural report of halogen...halogen “synthon crossover” in the self-assembly of coordination compounds has been published. Herein, we reported the structures of two coordination compounds containing *N*-(3-bromophenyl)pyridine-3-carboxamide flexible ligand, **L**^{3Br-nic}, which was obtained from the same starting materials and molar ratio under different crystallization temperature, scheme 1. The freedom of C-C and C-N single-bond rotation in the ligand gives rise to synthon crossover between type I and type II¹⁹ Br...Br interactions in these complexes.



Scheme 1. Synthetic strategy of [HgI₂(**L**^{3Br-nic})₂], **1**, and [HgI₂(**L**^{3Br-nic})], **2**.

Results and Discussion

Synthesis. The ligand, **L**^{3Br-nic}, was prepared by simply mixing the same equivalents of *meta*-bromoaniline and nicotinic acid in pyridine in the presence of triphenyl phosphite.²⁰ The reaction

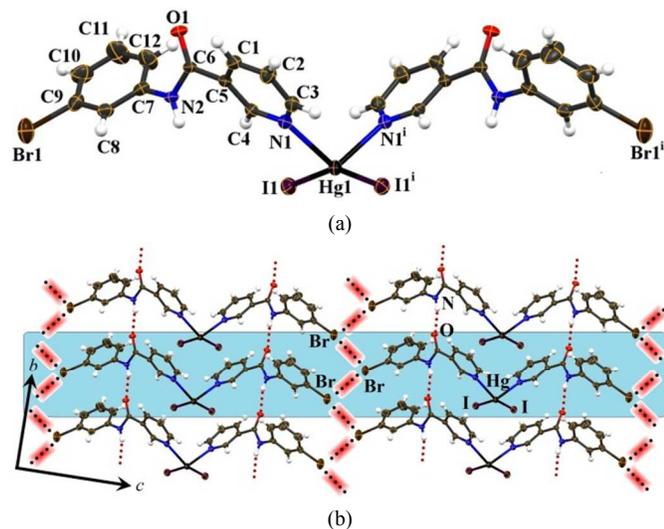


Figure 1. ORTEP of the structure of coordination compound formed between HgI_2 and $\text{L}^{3\text{Br-nic}}$, **1**, in room temperature (a), showing coordination geometry around central metal. Ellipsoids are drawn at 30% probability level. Generation of a wave-like chain, the blue ribbon, through the type II $\text{Br}\cdots\text{Br}$ halogen bonding interactions and cooperation of $\text{Br}\cdots\text{Br}$ contacts and $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonding to formation of 2D sheets, (b). Halogen bonds are shown in red. Symmetry code; (i) $-x, y, -z+1/2$.

of equimolar amount of ligand and HgI_2 in methanol affords a colorless solution. When the solution was left at room temperature, colorless needle crystals of $[\text{HgI}_2(\text{L}^{3\text{Br-nic}})_2]$, **1**, were obtained. On the other hand, when the reaction temperature was fixed at -4°C , crystals of $[\text{HgI}_2(\text{L}^{3\text{Br-nic}})]$, **2**, were obtained as colorless blocks. These two compounds were characterized by X-ray. It is notable that using a 2:1 molar ratio of the ligand and HgI_2 in room temperature resulted in the same product as when using a 1:1 molar ratio. Crystallographic data are listed in Table 1. Selected bond distances and angles are summarized in Table S1.

Structural analysis and investigation of temperature-dependent $\text{Br}\cdots\text{Br}$ synthon crossover in $[\text{HgI}_2(\text{L}^{3\text{Br-nic}})_2]$, **1, and $[\text{HgI}_2(\text{L}^{3\text{Br-nic}})]$, **2**.** X-ray structural analysis reveals that complex $[\text{HgI}_2(\text{L}^{3\text{Br-nic}})_2]$, **1**, crystallizes in one monoclinic space group $C2/c$, Table 1, and the asymmetric unit consists of a half of Hg^{2+} ion, one iodine atom and one $\text{L}^{3\text{Br-nic}}$ ligand. ORTEP view of this compound with atom labeling scheme is shown in Figure 1(a). According to the four-coordinate geometry index, τ_4 , defined by Houser and co-workers,²¹ the highly distorted tetrahedral geometry of the $\text{Hg}(\text{II})$ center can be better described as a seesaw structure, with a τ_4 value of 0.71. The I-Hg-I angle is $153.62(4)^\circ$, where the two Hg-I bonds form the plank (Hg-I : 2.6463(7) and 2.6464(7) Å, Table S1). The angle between the other two bonds (Hg-N : 2.510(7) Å and 2.511(7) Å, Table S1) which form the pivot is $106.0(3)^\circ$. The I-Hg-I and N-Hg-N planes are nearly perpendicular with a dihedral angle of $88.5(4)^\circ$. In complex **1**, individual molecules form a wave-like chain through the type II $\text{Br}\cdots\text{Br}$ halogen bonding interactions, Figure 1(b), blue ribbon. The distance of $\text{Br}\cdots\text{Br}$ interaction was found to be about 3.618(2) Å which is 2.2% shorter than the sum of the van der Waals radii of two bromine atoms, Table 2. According to the scatter plot derived from the CSD (version 5.35)²² for a correlation between $\text{C-Br}\cdots\text{Br-C}$ angles, θ_1 and θ_2 , for reporting structures containing intermolecular $\text{Br}\cdots\text{Br}$ halogen contacts below 3.70 Å (sum of Br van der Waals radii), Figure S1, the contact present in complex **1** is in the normal range for $\text{Br}\cdots\text{Br}$ contacts.

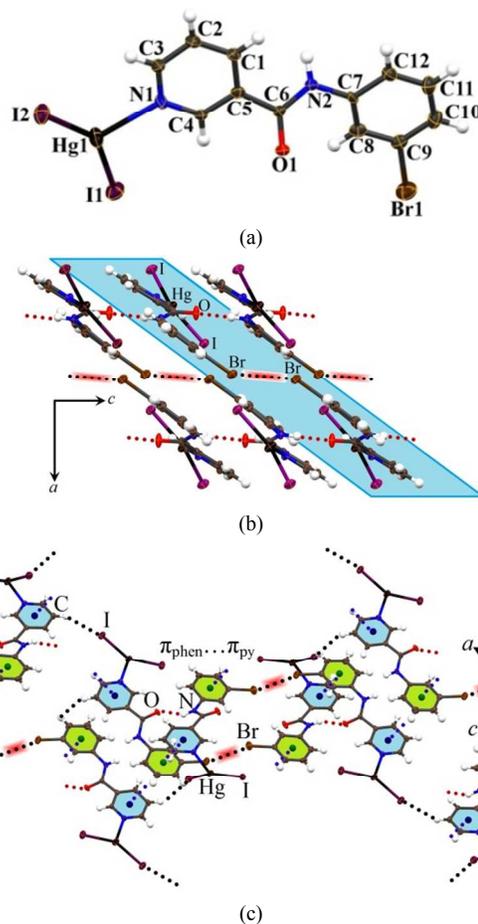


Figure 2. ORTEP of the structure of coordination compound formed between HgI_2 and $\text{L}^{3\text{Br-nic}}$, **2**, in -4°C (a), showing coordination geometry around central metal. Ellipsoids are drawn at 30% probability level. Generation of dimeric unit, the blue ribbon, through the Type I $\text{Br}\cdots\text{Br}$ interactions and formation of 2D sheets through the $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonds, (b). A side view representation of **2**, showing the cooperation of $\text{N-H}\cdots\text{O}=\text{C}$ and $\text{C}_{\text{py}}\text{-H}\cdots\text{I-Hg}$ hydrogen bonds and $\pi_{\text{phen}}\cdots\pi_{\text{py}}$ interaction, in generation of three dimensional packing, (c). Halogen...halogen interactions are shown in red.

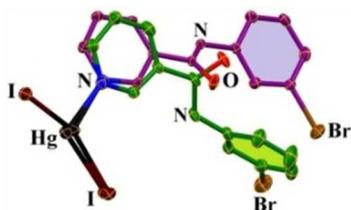
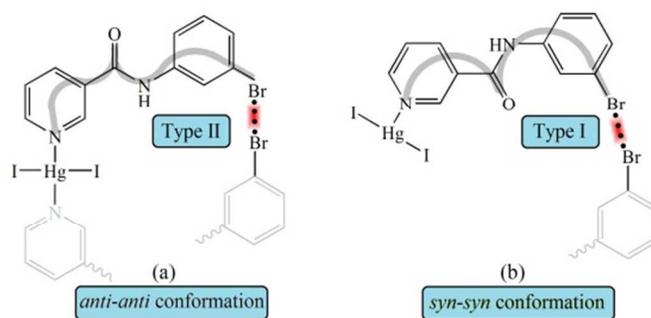
The resulting chains are further linked to each other by cooperation $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonding as main factor controlling the packing and $\text{Br}\cdots\text{Br}$ halogen bonds, Table S2, and form 2D sheets, Figure 1(b). In this compound, each Br acts as both halogen bond donor and an acceptor in the generation of bifurcated $\text{Br}\cdots\text{Br}$ halogen bonding interactions. Surprisingly, when the temperature was set at -4°C , block colorless crystals of $[\text{HgI}_2(\text{L}^{3\text{Br-nic}})]$, **2**, appeared in about one week. X-ray structural analysis of these crystals reveals that compound **2** has $C2/c$ space group, Table 1. The asymmetric unit of complex **2** consists of one Hg^{2+} ion, two iodine atoms, and one crystallographically independent ligand $\text{L}^{3\text{Br-nic}}$. As depicted in Figure 2(a), in this structure, the Hg atom is located in a three coordination environment and the coordination geometry is distorted trigonal-planar, with a trigonal-planar index, τ_3 ,²³ of 0.53. From complex **1** to complex **2**, the dramatic structural changes observed were clearly resulted from the different conformations adopted by flexible carboxamide ligands at various crystal growth temperatures. Since the pyridyl and bromophenyl rings are flexible in rotation around the $\text{C}_{\text{py}}\text{-CON}_{\text{amide}}$ and $\text{CON}_{\text{amide}}\text{-C}_{\text{phen}}$ bonds, this allows for subtle conformational adaptation of $\text{L}^{3\text{Br-nic}}$ to produce different interactions *via* the rotation of the rings. Figure 3 shows the $\text{Hg-I-N}_{\text{py}}$ -superimposed asymmetric units of complexes **1** and **2**.

Table 1. Structural data and refinement for complexes **1** and **2**.

	Complex 1	Complex 2
formula	C ₂₄ H ₁₈ Br ₂ HgI ₂ N ₄ O ₂	C ₁₂ H ₉ BrHgI ₂ N ₂ O
<i>fw</i>	1008.61	731.50
$\lambda/\text{\AA}$	0.71073	0.71073
<i>T</i> /K	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> /\AA	24.3489(18)	25.3903(15)
<i>b</i> /\AA	4.9200(6)	14.1304(6)
<i>c</i> /\AA	28.395(2)	9.1996(6)
$\beta/^\circ$	125.751(4)	99.658(5)
<i>V</i> /\AA ³	2760.6(4)	3253.8(3)
<i>D</i> _{calc} /Mg m ⁻³	2.427	2.987
<i>Z</i>	4	8
μ/mm^{-1}	10.735	15.7005
<i>F</i> (000)	1848	2592
2 $\theta/^\circ$	56.00	52.00
<i>R</i> (int)	0.1053	0.0985
GOOF	0.885	1.023
<i>R</i> ₁ ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0489	0.0640
<i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.1203	0.1406
CCDC No.	991771	991770

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \frac{[\sum (w(F_o^2 - F_c^2)^2)]^{1/2}}{[\sum w(F_o^2)]^{1/2}}$$

The conformational variations of the L^{3Br-nic} can be discussed by a dihedral angles of Hg-N_{py}-C=O and O=C-C9-Br that are 120.70(8)^o and 111.35(10)^o for **1** and 30.69(10)^o and 32.58(11)^o for **2**, respectively. According to these values, the L^{3Br-nic} ligand can be arranged in *anti-anti* and *syn-syn* conformations in **1** and **2**, respectively, scheme 2. In the presence of this flexibility, the bromine atom of the bromophenyl ring is pointed toward the adjacent molecule to generate different types of Br...Br synthons. Table 2 provides a summary of the geometrical parameter of the halogen bonding synthons observed in complexes **1** and **2**. As distinct to the packing described for complex **1**, in the crystal packing of complex **2**, a different type of Br...Br interaction is observed. In this complex, two independent moieties are closely packed through Type I Br...Br contacts, Table 2, to generate dimeric units, Figure 2(b), blue ribbon. The distance of Br...Br interaction was found to be about 3.391(2) \AA which is 8.2 % shorter

**Figure 3.** The asymmetric units of compounds **1** (green) and **2** (violet) superimposed to illustrate the conformational freedom of the flexible carboxamide ligand.**Scheme 2.** *Anti-anti* and *syn-syn* conformations of L^{3Br-nic} and halogen...halogen synthons exhibited in Hg(II) complexes.

than the sum of the van der Waals radii of two bromine atoms. According to the scatter plot derived from the CSD, Figure S1, the contact present in complex **2** is in the normal range for type I Br...Br interactions. Adjacent dimeric units are further linked to each other by head-to-tail N-H...O=C hydrogen bonds as main factor controlling the packing to generation 2D sheets in *ac*-plane, Figure 2(b), Table S2. These hydrogen bonds are cooperates with $\pi_{\text{phen}} \cdots \pi_{\text{py}}$ interaction, Figure 2(c), Table S2. In the packing of this complex, the overall supramolecular structure results from the C_{py}-H...I-Hg hydrogen bond, Figure 2(c), Table S2.

Furthermore, the intermolecular contacts in these crystal structure of these compounds are quantified *via* Hirshfeld surface analysis²⁴ using CrystalExplorer 3.0.²⁵ These surfaces visually summarize the spatial arrangement and relevance of intermolecular interactions by their color code. The percentage contributions of intermolecular contacts are shown in Figure 4, as pie-charts. These charts indicate that the H...H and H...X (X = Br and I) interactions are indeed the dominating one, while only 3.0% and 2.0% contribution comes from the type I and type II weak Br...Br interactions. Weak intermolecular interactions such as Br...Br are not the only interaction between molecular units, but they play an important role in holding the molecules together.

The binding energies obtained from DFT on two relative fragments provide us an opportunity to evaluate these halogen...halogen interactions. Calculations were performed with the experimental structures as the starting point at the LDA-ZORA/TZP level. The outcomes obtained from DFT methods are listed in Table 2. From these data, it is explicit that the Br...Br interaction energy about -6.93 and -17.8 kJ.mol⁻¹, which is in the range of weak halogen bonding interaction energies.²⁶

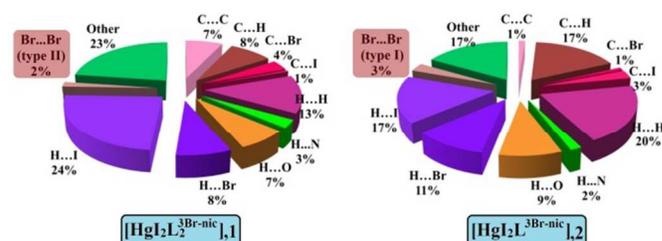
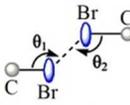
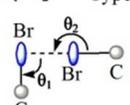
**Figure 4.** Relative contributions of various intermolecular contacts to the Hirshfeld surface area in compounds **1**, left, and **2**, right.

Table 2. Geometrical parameters (Å and °) for the description of the Br...Br halogen bonding, calculated XB binding energies (LDA-Zora/TZP), conformational parameters, coordination geometries and τ_i values of complexes **1** and **2**.

	Complex 1	Complex 2	Definition of geometrical Br...Br parameters
Br...Br	3.618(2)	3.391(2)	
θ_1	107.7(3)	148.7(3)	
θ_2	166.6(3)	148.7(3)	
Type	II	I	$\theta_1 = \theta_2$ Type I
Change of sum of vdW radii (%)	2.2	8.2	
Coordination geometry/ τ_i	Seesaw/ $\tau_4=0.71$	trigonal-planar/ $\tau_3=0.53$	
$L^{3Br-nic}$ conformation	<i>anti/anti</i>	<i>syn-syn</i>	$\theta_1 = 90^\circ$ $\theta_2 = 180^\circ$ Type II
Calculated XB energy(kJ/mol)	-6.93	-8.90	
Sym. code	-x- 1/2,y+1/2, -z-1/2	-x+1, y, -z+5/2	

Conclusion

In this study, the temperature-dependent synthon crossover has been investigated in two mercury coordination compounds containing *N*-(3-bromomethyl)-2-pyridinecarboxamide flexible ligand. The crossover between type I and type II Br...Br synthons on the formation of coordination compounds has been investigated for the first time. From our results, it can be seen that different type of Br...Br synthons, along with other intermolecular interactions, result in the formation of complexes with different network structures and different chemical compositions even from the same amount of reagents. Further studies are in progress to synthesize new complexes from other flexible carboxamide ligands based on this approach.

Experimental Section

Chemicals and instrumentation. All solvents such as methanol and pyridine and the chemicals were commercially available (reagent grade) and were purchased from Merck and Aldrich and used without further purification. Infrared spectra (4000–400 cm^{-1}) of solid samples were taken as 1% dispersion in KBr pellets using a BOMEM-MB102 spectrometer. ^1H NMR spectra were recorded on a Bruker AC-300 MHz spectrometer at ambient temperature in CD_3OD . All chemical shifts are quoted in part per million (ppm) relative to tetramethylsilane. Melting point was obtained by a Bamstead Electrothermal type 9200 melting point apparatus and corrected.

Single crystal diffraction studies. For these compounds the intensity data were collected on a STOE IPDS-II or STOE-IPDS-2T diffractometers with graphite monochromated Mo- $K\alpha$ radiation, 0.71073 Å. Data were collected at a temperature of 298(2) K in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA²⁷ software package. A numerical absorption correction was applied using X-RED²⁸ and X-SHAPE²⁹ software's. All the structures were solved by

direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using the SHELXL-97 program package³⁰. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$. All the refinements were performed using the X-STEP³² crystallographic software package³¹. Structural illustrations have been drawn with MERCURY³² windows. Crystallographic details including crystal data and structure refinement are listed in Table 1.

Synthesis of *N*-(3-bromophenyl)-pyridine-3-carboxamide. This compound was prepared by simply mixing the same equivalents of *para*-bromoaniline and nicotinic acid in pyridine in the presence of triphenyl phosphite, according to what has been reported previously.⁴⁰ The *N*-(3-bromophenyl)-pyridine-3-carboxamide compound was prepared by the reaction of 3-bromoaniline (5 mmol) and nicotinic acid (5 mmol) in pyridine under the boiling point and in reflux condition. The resulting solution was stirred at 313 K for 20 min, then triphenyl phosphite (5 mmol) was added dropwise, and the reaction mixture was stirred 5 h at 373 K and 24 h at ambient temperature. The mixture was added to 200 ml distilled water. Precipitation of a white solid resulted with a yield of 85%, which was filtered off and dried under reduced pressure. (melting point = 185 °C). Anal. calcd for $\text{C}_{12}\text{H}_9\text{BrN}_2\text{O}$: C, 61.95; H, 3.87; N, 12.03. Found: C, 61.99; H, 3.91; N, 12.08. FT-IR (KBr pellet, cm^{-1}): 3322, 1672, 1596, 1477, 1315, 1110, 864, 690, 621, 420. ^1H NMR (CDCl_3 , δ from TMS): 9.15 (1H-pyridine), 8.80 (1H-pyridine), 8.44 (1H-pyridine), 8.10 (1H-phenyl), 7.73-7.70 (2H-pyridine and phenyl), 7.36-7.31 (2H-phenyl).

Synthesis of $[\text{HgBr}_2(\text{L}^{3Br-nic})_2]$, **1 and $[\text{HgBr}_2(\text{L}^{3Br-nic})]$, **2**.** To a solution of HgBr_2 (0.1 mmol), in 3 mL methanol, a solution of $\text{L}^{3Br-nic}$ (0.1 mmol) in 3 mL methanol was added with stirring. The mixture was heated at 40 °C for about 1 h and then filtered. Upon slow evaporation of the filtrate at room temperature, suitable crystals of complex **1** for X-ray analysis were obtained after 10 days (yield 65%, m.p. = 188-190 °C). Anal. calcd for $\text{C}_{24}\text{H}_{18}\text{Br}_2\text{HgI}_2\text{N}_4\text{O}_2$: C, 28.55; H, 1.78; N, 5.55. Found: C, 28.58; H, 1.83; N, 5.59. FT-IR (KBr pellet, cm^{-1}): 3261, 1646, 1583, 1304, 1037, 775, 624, 427. ^1H NMR (CDCl_3 , δ from TMS): 9.00 (1H-pyridine), 8.64 (1H-pyridine), 8.31 (1H-pyridine), 7.88 (1H-phenyl), 7.57-7.49 (2H-pyridine and phenyl), 7.34-7.15 (2H-phenyl).

Upon slow evaporation of the filtrate at -4 °C, suitable crystals of complex **2** for X-ray analysis were obtained after on2 week (yield 71%, m.p. = 192-194 °C). Anal. calcd for $\text{C}_{12}\text{H}_9\text{BrHgI}_2\text{N}_2\text{O}$: C, 19.69; H, 1.23; N, 3.83. Found: C, 19.72; H, 1.27; N, 3.86. FT-IR (KBr pellet, cm^{-1}): 3256, 1651, 1585, 1520, 1304, 1188, 1033, 682. ^1H NMR (CDCl_3 , δ from TMS): 9.10 (1H-pyridine), 8.72 (1H-pyridine), 8.30 (1H-pyridine), 7.91 (1H-phenyl), 7.60-7.55 (2H-pyridine and phenyl), 7.40-7.08 (2H-phenyl).

Computational details. DFT calculations were performed using the ORCA quantum chemistry suite.³³ The local spin density approximation (LSD) exchange correlation potential was used with the Vosko-Wilk-Nusair (VWN) local density potential.³⁴ Gradient-corrected geometry optimizations³⁵ were performed by using the generalized gradient approximation (Perdew-Wang non-local exchange and correlation corrections – PW91).³⁶ The selected two fragments were cut out directly from the CIF data without optimization, and so, without geometrical parameters changing. Large atom basis sets TZP, triple- ξ Slater type orbital with one set of polarization functions, are used to ascribe all the atoms here. A frozen core approximation was used to treat the core electrons: (1s) for C and N, (4p) for I, (3p) for Br and (1s) for O. Scalar relativistic

effects were taken into account by using the zeroth-order regular approximation (ZORA).³⁷

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Notes and references

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† Selected bond distances and bond angles, hydrogen bonding and $\pi\cdots\pi$ interactions parameters. These materials available free of charge via the Internet at <http://pubs.rsc.org>.

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Temperature-dependent halogen...halogen synthon crossover in coordination compounds

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The temperature-dependent Br...Br halogen...halogen synthon crossover in two coordination compounds of HgI_2 and *N*-(3-bromophenyl)pyridine-3-carboxamide flexible ligand, $\text{L}^{3\text{Br-nic}}$, have been investigated. Results show that when starting with equivalent amount of reagents and when the reaction was carried out at room temperature, a 1:2 adduct of the $\text{HgI}_2:2\text{L}^{3\text{Br-nic}}$, complex **1**, was generated, whereas when the reaction temperature was fixed at $-4\text{ }^\circ\text{C}$, a 1:1 adduct, complex **2**, was obtained. In **1**, individual molecules form a wave-like chain through the type II Br...Br halogen bonding interactions, while Br...Br interaction generates dimeric units in **2**.

