

Halogen Bonding Synthon Modularity in Coordination Compounds

Hamid Reza Khavasi,* Fataneh Norouzi, and Alireza Azhdari Tehrani

Faculty of Chemistry, Shahid Beheshti University, G. C., Evin, Tehran 1983963113, Iran

Supporting Information



ABSTRACT: In this Communication, the modulation of halogen bonding synthons in the crystal structure of $[HgBr_2(L^{3,4-diCl})]$ from $[HgBr_2(L^{3-Cl})]$ and $[HgBr_2(L^{4-Cl})]$, as single components, where L is a N-(chlorinatedphenyl)-2-pyrazinecarboxamide ligand, has been investigated. Reviewing the crystal packing reveals that Cl…N and Cl…Br halogen bonds stood as a remembrance of the crystal structures of single components in the packing of $[HgBr_2(L^{3,4-diCl})]$.

he overall ambition of crystal engineering is the synthesis of designed crystalline molecular structures with desired properties.¹⁻⁴ In this regard, a molecular structure can be defined as a multisegment subject, where each segment, as a single molecular component, carries one or more functional groups, and so its crystal packing is involved in one or more intermolecular synthon. Synthon modularity 5-7 is the presence of synthon repetitivity between functional groups of a molecular structure and functional groups of its segments. Since the final crystal packing may be defined based on the gathering of different synthons from different segments, synthon modularity is rare and there are limited examples reported in the literature. In a recent paper by Desiraju,⁸ cocrystals of 4-hydroxybenzamide with aliphatic dicarboxylic acids based on strong hydrogen bonding synthon modularity have been reported. The modulation of O-H…N synthons in the systematic cocrystallization of mono-, di-, and trihydroxybenzoic acids with hexamine was investigated by Guru Row and coworkers in 2014.9 In contrast to the presence of different interactions in the formation of co-crystals, reports on synthon modularity in cocrystals based on halogen bond interactions¹⁰ are rare. Desiraju and his co-workers also described the design of binary¹¹ and ternary¹² co-crystals based on hydrogen bond and halogen bond synthon modularity. The crystal packing of 4-bromobenzamide-n-alkyldicarboxylic acid co-crystals, shows that O-H…O hydrogen bonds are reminiscence of the crystal structure of dicarboxylic acid while type I and type II Br…Br interactions are similar to the crystal structure of 4bromobenzamide. Furthermore, the modulation of the O-H…O hydrogen bonds and Br/I…O2N halogen bonds in ternary co-crystals of 4-benzamide-dicarboxylic acid-dinitroben-

zene has recently been reported.¹² In 2011, the structural modularity in 2,3,4- and 3,4,5-trichlorophenol was reported by Mukherjee and Desiraju.7 Inspection of the crystal packing showed that the crystal structure of these chlorinated phenols contains Cl---Cl interaction and hydrogen bonding patterns that occur in the structures of monochlorophenol and dichlorophenol. In spite of these reports on modularity in the crystal structures of individual molecules, including chlorinated phenols, and co-crystals of organic compounds,^{7-9,11} to the best of our knowledge, the study of the synthon modularity in the crystal structure of coordination compounds has not been thoroughly discussed. As part of our effort for the investigation of the effect of the weak intermolecular interactions in the crystal packing of mercury coordination compounds including pyrazine/pyridine carboxamide ligands,^{13–17} halogen bonding synthon modularity in coordination compounds has herein been reported for the first time. In the present study, three N-(chlorinatedphenyl)-2-pyrazinecarboxamide ligands, L^{3-Cl}, L^{4-Cl}, and L^{3,4-diCl} (Scheme 1), carrying chlorine atoms in phenyl meta- or/and para-positions, have been employed for the synthesis of mercury(II) bromide complexes. Examining the crystal packing of $[HgBr_2(L^{3,4-diCl})]$ clearly shows that the Cl… N and Cl…Br halogen bonding synthons are a remembrance of the crystal structures of $[HgBr_2(L^{3-Cl})]$ and $[HgBr_2(L^{4-Cl})]$, respectively, as single components. It should be noted that complex 1 has been previously reported by some of us,¹⁶ but here, we present a comparative study of this crystal structure

Received: February 26, 2015 Revised: April 19, 2015

Scheme 1. Synthesized Complexes	$[HgBr_2(L^{3-Cl})], 1$
$[HgBr_2(L^{4-Cl})]$, 2, and $[HgBr_2(L^{3,4-c})]$	diCl)], 3

$Br \xrightarrow{Hg} N \xrightarrow{N} H$				
Complex	X1	X2		
$[HgBr_2(L^{3-Cl})], 1$	Cl	Н		
$[HgBr_2(L^{4-Cl})], 2$	Н	Cl		
$[HgBr_2(L^{3,4-diCl})], 3$	Cl	Cl		

with the other two new structures, complexes 2 and 3, for studying the synthon modularity. Our opinion is that the results of the present study can be helpful in crystal engineering especially in the crystal structure prediction research field. The ligands, L^{3-Cl} , L^{4-Cl} , $L^{3,4-diCl}$, were synthesized by the

reaction of 3-chloroaniline, 4-chloroaniline, or 3,4-dichloroaniline and pyrazinecarboxylic acid in 1:1 ratio and in the presence of triphenyl phosphite (for details of the experimental procedures, see the Supporting Information).^{18,19} A reaction between methanolic solutions of HgBr₂ and these ligands in 1:1 ratio afforded air-stable plate, prism, and block crystals of $[HgBr_2(L^{3-Cl})]$, 1, $[HgBr_2(L^{4-Cl})]$, 2, and $[HgBr_2(L^{3,4-diCl})]$, 3, respectively, after a few days. A summary of the crystallographic data and structure refinement is listed in Table S1. Selected lengths and angles with estimated deviations are summarized in Table S2. X-ray diffraction analysis ascertains that all complexes crystallized in orthorhombic crystal system with space group of *Cmca* for **1** and **3** and *Pbca* for **2** (Table S1). The asymmetric unit of these compounds comprises two bromine atoms, one Hg²⁺ ion, and one crystallographically independent ligand. ORTEP drawings with the atom labeling schemes used for compounds 2 and 3 are shown in Figure S1. In all three structures, the central metal atom is three-coordinated and lies in a T-shaped geometry formed by one pyrazine nitrogen atom of ligand and two bromine atoms. These compounds have a trigonal-planar index, τ_{3} ,¹⁶ of 0.32, 0.21, and 0.23, respectively. Inspection of the crystal structure of these compounds reveals that the packing difference between them can be discussed by considering intermolecular interactions in the b-direction. In complex 1, individual molecules form a linear chain in the bdirection by Cl…N halogen bonds (Figure 1 (up) and Table 1). The Cl…N distance is 3.217(5) Å, and so is 2.5% shorter than the sum of van der Waals radii of chlorine and nitrogen atoms.²⁰ The angle of C-Cl···N is 163.5 $(5)^{\circ}$ which is in accordance with $n_{(nitrogen)} \rightarrow \sigma^*_{(chlorine)}$ electron donation.²¹ These halogen bonds are accompanied by the weak hydrogen bonds between the C-H donor and the carbonyl oxygen acceptor (Figure 1 (up) and Table 1). In complex 2, individual units are closely packed through $C-Cl\cdots Br-Hg$ contacts (Figure 1 (down), Table 1) to generate a 1D chain in the *b*direction. The distance of Cl-Br contacts was found to be about 3.548(4) Å, which is 1.4% shorter than the sum of the van der Waals radii of chlorine and bromine atoms.²⁰ There are also C-H…Cl weak hydrogen bonds that cooperate in the



Figure 1. Side view representation of complexes 1-3 in *a*-direction, illustrating the presence of Cl···N halogen bonds, XB_{CIN} synthon (red-highlighted) in 1, (up), the presence of Cl···Br halogen bonds; XB_{CIBr} synthon (green-highlighted) in 2, (down), and modulation of both halogen bonds in 3, (middle).

halogen bonding interactions (Table S3). In complex 3, in the *b*-direction, there are two different halogen bonding synthons, XB_{CIN} , Cl…N, and XB_{CIBr} , Cl…Br. The distance of XB_{CIN} and XB_{CIBr} contacts was found to be about 2.967(6) and 3.477(5) Å, respectively, which is 10.1% and 3.4% shorter than the sum of the van der Waals radii of chlorine and nitrogen/bromine atoms²⁰ (Table 1). In this complex, adjacent molecules are linked to each other through these XB synthons with the cooperation of N–H…Cl and C–H…O=C hydrogen bonds, to generate linear chains in the *b*-direction, similar to complexes 1 and 2 (Figure 1 (middle), Table S3). As indicated in Figure 1, synthon XB_{CIBr} is modulated from 2 to 3. Therefore, the metachloro and para-chloro positions in 3 play the same roles as they do in 1 and 2, individually. These structural correlations

Table 1. Halogen Bond Parameters and Calculated BindingEnergies for Complexes 1–3

complex	1^{a}	2	3
Cl…N (Å)	$3.217(5)^{c}$	-	$2.967(6)^{c}$
Cl…Br (Å)	-	$3.548(5)^d$	$3.477(5)^e$
C-Cl…N (deg)	163.5(5)	-	179.4(6)
C-Cl…Br (deg)	-	122.1(5)	130.7(6)
Hg-Br…Cl (deg)	-	169.7(1)	166.2(5)
Reduction of the sum of the vdW radii (%)	2.5	1.4	10.1, 3.4 ^f
Binding energy (kJ/mol) ^b	-31.10	-30.53	-36.70

^{*a*}From ref 16. ^{*b*}The values are related to the energy of the interaction between two adjacent fragments (Figure S2). ^{*c*}1–*x*, 1/2+*y*, 1/2–*z*. ^{*d*}–*x*, -1/2+y, 1/2-z. ^{*d*}–*x*, -1/2+y, 1/2-z. ^{*c*}1–*x*, -1/2+y, 1/2-z. ^{*f*}These values are related to Cl…N and Cl…Br halogen bonds, respectively.

provide a unique example of the structural modularity in coordination compounds based on halogen bonding interactions. In these complexes, linear chains are linked together through head-to-tail $\pi_{\rm phen}$ ····-NHCO- interactions in *a*direction to generate 2D sheets (Figure 2, Table S3). In the packing of these complexes, the overall supramolecular assemblies result from the linkage of 2D sheets by Hg···Br contacts (Figure 2, Table S3). The Hg···Br contacts of 3.401(1), 3.367(5), and 3.414(6) Å for 1-3, respectively, are comparable to those previously reported.^{16,22} Conformational adaptation of the ligands for the generation of different conformers in the packing of crystals 1-3, is allowed due to the flexibility of the chlorinated ligands for rotation around the C_{pyz}-CON_{amide} bonds. This flexibility has been shown in our previous reports for similar carboxamide ligands.^{13,16,23,24} As indicated in Figure 3, which shows the HgBr₂-Pyz-super-imposed units of complexes 1-3, all three ligands have the



Figure 3. Asymmetric units of compounds 1 (green), 2 (violet), and 3 (red) superimposed to illustrate the conformational freedom of the flexible carboxamide ligand.

same conformation. Moreover, in all three complexes pyrazine and phenyl rings are in-plane with the maximum deviation of less than 9° for complex **2**. These structural similarities can reinforce the modulation of different synthons of **1** and **2** into the structural packing of **3**.

Qualitative support for this similarity is afforded by comparing the electrostatic potential maps for compounds 1-3 (Figure 4). These electrostatic potential maps show that, although the presence of two chlorine atoms on the aromatic ring causes complex 3 to essentially have lower negative electrostatic potentials above and below the phenyl ring, compared to 1 and 2, according to the side view representation of the halogen σ -hole, shown on the right side of each MEP, it can be concluded that chlorine atoms in both meta and para positions have nearly the same participation in the halogen bonding interaction. These intermolecular interactions can also be quantified via Hirshfeld surface analysis study. The contributions of Hg…Br, π …amide, Cl…N, and Cl…Br contacts to the Hirshfeld surface areas are illustrated in Figure 5. As clearly shown by this histogram, Hg…Br and π …amide contacts have nearly the same contribution in all complexes. In complex 1, the Cl...N halogen bond contributes by 1.4%. From 1 to 2,



Figure 2. Generation of 2D sheets through head-to-tail π_{phen} ...(NHCO) interactions (pink ribbon) in *a*-direction and formation of overall supramolecular assemblies from the linkage of 2D sheets by Hg...Br contacts (gray ribbon) in complex 1, left side, and complex 3, right side. Different colors show different adjacent linear chains. XB_{ClBr} and XB_{ClN} synthons are red- and green-highlighted, respectively.



Figure 4. Electrostatic potentials mapped on the electron isodensity surface of **1** (a), **2** (b), and **3** (c) at the same contour value of 0.008 electron per Bohr.³ Areas of high electron density are shown as red and low electron density as blue. The side view representation of chlorine σ -hole is shown on the right side of each electrostatic potentials map.



Figure 5. Selected contribution percentages of Hg···Br, π ···amide, Cl··· N, and Cl···Br contacts in the crystal packing of complexes 1–3. π ··· amide considered as the sum of C···N and C···O contacts. Data for complex 1, is calculated using CIF file with CSD entry code of QEZPOC, reported in ref 16.

by changing the chloro-position, the contribution of the Cl…N halogen bonds decreased to 0.0%, and the chlorine atom was

involved in the Cl…Br halogen bond with a contribution of 5.6%. In complex 3, the contribution of both XB contacts, 4.4% and 5.7% for Cl…N and Cl…Br, respectively, was observed.

Furthermore, the evaluation of these halogen bonding interactions involving synthon modularity can be done by DFT-calculation of the binding energies between two relative fragments. Theoretical calculations were achieved at the LDA-ZORA- TZP level on fragments directly cut out from the experimental data. Calculated binding energies are listed in Table 1. This data shows that binding energies between two adjacent fragments involving halogen bonding interactions ranges from -30.53 to -36.70 kJ mol⁻¹. Based on strength and directionality, it can be concluded that these halogen bonds, XB_{CIN} and XB_{CIBr}, play an important role in determining the final supramolecular structures.

In conclusion, modulation of halogen bonding synthons in the crystal structures of $HgBr_2$ complexes of *N*-(chlorinated-phenyl)-2-pyrazinecarboxamide ligands have been investigated. Results clearly show that in the crystal packing of $[HgBr_2(L^{3,4-diCl})]$, the Cl…N and Cl…Br halogen bonds are reminiscent of the crystal packing of $[HgBr_2(L^{3,Cl})]$ and $[HgBr_2(L^{4-Cl})]$, respectively, as single components. This study is the first report on structural modularity in coordination compounds, and can be useful in different branches of inorganic crystal engineering such as polymorphism and crystal structure prediction.

ASSOCIATED CONTENT

S Supporting Information

Experimental details, the ORTEP diagram, fragments selected for calculation of dimer binding energies, crystallographic data, selected bond distances and bond angles, and intermolecular interaction parameters. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b00282.

AUTHOR INFORMATION

Corresponding Author

*E-mail: h-khavasi@sbu.ac.ir.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We would like to thank Graduate Study Councils of Shahid Beheshti University, General Campus for financial support.

REFERENCES

(1) Desiraju, G. R. Crystal Engineering. The Design of Organic Solids; Elsevier: Amsterdam, 1989.

(2) Grepioni, F.; Braga, D. Making Crystals by Design-From Molecules to Molecular Materials, Methods, Techniques, Applications; Wiley-VCH: Weinheim, Germany, 2007.

(3) Desiraju, G. R. *The Crystal as a Supramolecular Entity;* John Wiley & Sons: New York, 1996.

(4) Steed, J. W.; Atwood, J. L. Supramolecular Chemistry; Wiley: Chichester, 2000.

- (5) Desiraju, G. R. J. Am. Chem. Soc. 2013, 135, 9952-9967.
- (6) Mukherjee, A.; Tothadi, S.; Desiraju, G. R. Acc. Chem. Res. 2014, 47, 2514–2524.

(7) Mukherjee, A.; Desiraju, G. R. Cryst. Growth Des. 2011, 11, 3735–3739.

(8) Tothadi, S.; Desiraju, G. R. Cryst. Growth Des. 2012, 12, 6188-6198.

Crystal Growth & Design

- (9) Kaur, R.; Lalithalakshmi, B. V.; Guru Row, T. N. Cryst. Growth Des. 2014, 14, 2614–2620.
- (10) Desiraju, G. R.; Ho, P. S.; Kloo, L.; Legon, A. C.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. *Pure Appl. Chem.* **2013**, *85*, 1711–1713.
- (11) Tothadi, S.; Joseph, S.; Desiraju, G. R. Cryst. Growth Des. 2013, 13, 3242-3254.
- (12) Tothadi, S.; Sanphui, P.; Desiraju, G. R. Cryst. Growth Des. 2014, 14, 5293-5302.
- (13) Khavasi, H. R.; Esmaeili, M. CrystEngComm 2014, 16, 8479–8485.
- (14) Khavasi, H. R.; Mir Mohammad Sadegh, B. Dalton Trans. 2014, 43, 5564–5573.
- (15) Khavasi, H. R.; Azhdari Tehrani, A. CrystEngComm 2013, 15, 5799-5812.
- (16) Khavasi, H. R.; Azhdari Tehrani, A. Inorg. Chem. 2013, 52, 2891–2905.
- (17) Khavasi, H. R.; Azizpoor Fard, M. Cryst. Growth Des. 2010, 10, 1892–1896.
- (18) Sasan, K.; Khavasi, H. R.; Davari, M. D. Monatsh. Chem. 2008, 139, 773–780.
- (19) Khavasi, H. R.; Azhdari Tehrani, A. CrystEngComm 2013, 15, 3222-3235.
- (20) Bondi, A. J. Phys. Chem. 1964, 68, 441-451.
- (21) Ananthavel, S. P.; Manoharan, M. Chem. Phys. 2001, 269, 49-57.
- (22) Wu, J.-Y.; Hsu, H.-Y.; Chan, C.-C.; Wen, Y.-S.; Tsai, C.; Lu, K.-L. *Cryst. Growth Des.* **2009**, *9*, 258–262.
- (23) Khavasi, H. R.; Ghanbarpour, A.; Azhdari Tehrani, A. *CrystEngComm* **2014**, *16*, 749–752.
- (24) Khavasi, H. R.; Azhdari Tehrani, A. CrystEngComm 2013, 15, 5813–5820.