Triiodide-Based Chair-Like Copper Complex Assembled by Halogen Bonding

Mikhail A. Kinzhalov,* Ekaterina I. Kinzhalova, Valentina A. Karnoukhova, Ivan V. Ananyev, Rosa M. Gomila, Antonio Frontera, Vadim Yu. Kukushkin, and Nadezhda A. Bokach*



1. INTRODUCTION

architecture of $5.2I_2$.

Although the definition of halogen bonding (abbreviated as HaB; for recent reviews, see refs 1-3) was formalized by the IUPAC only a decade ago (2013),4 the phenomenon of noncovalent interatomic bonding involving electron-accepting halogen atoms was recognized much earlier under the framework of "charge-transfer interactions". One of the first documented examples is the solid-state X-ray structure of a 1:1 dioxane-bromine adduct (Figure 1) studied by Odd Hassel.⁵ In this structure, infinite chains made of alternating molecules of Br₂ and 1,4-dioxane were held together in modern terms by HaB; molecules of dioxane were stabilized in the chair conformation. For his contribution to the development of the concept of conformation, Hassel (jointly with D. Barton) was awarded the Nobel Prize in Chemistry in 1969. On the other hand, his attention to HaB between Br and O centers in the same dioxane-bromine structure went almost unnoticed by the chemistry community until the publication of seminal reviews by Metrangolo and Resnati (see refs 6-8 and references therein). We report herein a completely different pattern of inorganic chair structures also held by HaB. In this novel supramolecular motif, the triiodide-based chair-like $Cu_2(\mu-I_3)_2$ complexes are linked by HaB with incorporated iodine molecules, accomplishing chained arrays (Figure 1).

Following our recent work on noncovalent interactions in organometallics, in particular HaB including iodine and polyiodides,^{9–11} we studied crystallization and solid-state structures of adducts of $[CuI(CNR)_2]_n$ (n = 2, R = Xyl; $n = \infty$, C_6H_3 -2-Cl-6-Me) with I_2 , a strong HaB donor. In the $[CuI(CNXyl)_2]_n/I_2$ system, we obtained a $(XylNC)Cu^I$



Figure 1. HaB-based chains composed of Br₂ and 1,4-dioxane molecules (Hassel's organic chair; left panel) and of I₂ and $[Cu_2(\mu-I_3)_2(CNXyl)_4]$ (inorganic chair identified in this work; right panel).

Received:August 29, 2023Revised:November 21, 2023Accepted:November 30, 2023Published:December 18, 2023



assembly



2. RESULTS AND DISCUSSION

2.1. Polyiodide Copper(I) Complexes. Polyhalides are a subject of intensive studies^{12–14} and these species found various applications as electrolytes for batteries and also for dye-sensitized solar cells,^{12,13} mild selective oxidants for organic synthesis,¹³ and synthons for the construction of metal–organic frameworks.¹⁵ Metal polyhalide complexes, namely species bearing metal–halogen coordination or semicoordination bonds, have been attracting increasing interest for the past decade; the recent review¹⁵ summarizes advances in the chemistry of metal polyhalides, indicating, in particular, that polyiodides are substantially more abundant than polybromides, while the number of studied polychlorides (for the relevant literature, see refs 16–20) is rather small.

Copper complexes, among other transition metal compounds, demonstrate wealth and versatility of their polyiodide chemistry.¹⁵ As far as copper(I) polyiodides are concerned, the adduct $[Cu_2(\mu_4-L)(\mu_2-I)(I_2)(I_3)]_n \cdot nI_2$ (L = 1-tetrazole-4imidazole-benzene) forms a three-dimensional (3D) network built by one-dimensional (1D) coordination polymer chains, which are halogen-bonded by I2.21 Other examples of copper(I) and mixed valent copper(I/II) species include the binuclear $[Cu_2I_2(ttab)]$ (ttab = 1,2,4,5-tetra(7-azaindol-1yl)benzene),²² [Cu₂(I₃)₂(ttab)],²² trinuclear [Cu₃(μ -I)₂(κ ¹- $I_{3}_{2}(L')_{2}_{n}$ (L' = 1-(4,5-dihydro-3-propyl-imidazolidin-2-yl)-3-propyl-imidazolidine-2-thione),²³ and heterometallic $[Mo_2O_2S_6Cu_6(\mu-I_2)(4,4'-bipy)_3]_n \cdot nH_2O$ compounds.²⁴ Metal-organic frameworks, featuring halogen-bonded I2 or ICl, such as $[Cu(\mu_2(I^1,I^3)-I_3)\{\mu_2-(3,3',5,5'-\text{tetramethy})-4,4'$ bipyrazole)}]_n, $[Cu(\mu_2(I^1,I^1)-I_3)\{\mu_2-(3,3',5,5'-\text{tetramethyl-}$ 4,4'-bipyrazole)}]_n, and $[Cu(\mu_2(I^1,I^1)-I_2Cl){\mu_2-(3,3',5,5'-tetra$ methyl-4,4'-bipyrazole)}]_n were studied by X-ray diffractometry (XRD).²⁵ As can be inferred from these considerations, (polyiodide)Cu^I species are mostly represented by triiodides and supporting organic ligands include N- and S-coordinated mono- and bidentate species.

Although strong π -back-donating isocyanide ligands²⁶ similar to other complexes of low-oxidation state metal centers²⁷ are able to stabilize the copper(I) oxidation state, (RNC)Cu^I-based polyhalides are still little explored. We recently obtained the polyhalide adducts [Cu(I₃)(CNXyl)₃], [Cu(I₃)(CNXyl)₃]·¹/₂I₂, and [Cu(CNXyl)₃](I₅) from [CuI-(CNXyl)₃] and I₂; these species are formed depending on the molar ratio between the reactants.²⁸ In view of our interest in isocyanide chemistry (for review, see ref 26; for recent works, see refs 29 and 30 and references therein), copper(I) chemistry, and the supramolecular chemistry of polyhalides (for recent works, see refs 10, 11, and 28), the idea of a study that combines all three areas seemed to be attractive.

2.2. Cocrystallization of $CuX(CNR)_2$ Complexes with I_2 . In continuation of our studies of HaB-based supramolecular organization of (poly)iodides $(CNR)_nCu^{I,11,28}$ for this work, we addressed copper(I) complexes exhibiting 1:2 ratio between copper and isocyanide ligands. We prepared two complexes having the empirical formula $CuI(CNR)_2$ (R = Xyl 1, 92%; C_6H_3 -2-Cl-6-Me 2, 95%) by the reaction of CuI with CNR (1:2 molar ratio; 20 °C, 40 min; see the Experimental

Section). Although the formulas are the same, the structures of the species are different. According to the XRD studies, **1** was identified as the dimeric $[Cu_2(\mu-I)_2(CNXyl)_4]$, while **2** as the polymeric *catena*- $[Cu(\mu-I)(CNC_6H_3-2-Cl-6-Me)_2]$ complex (Figure 2).



Figure 2. Molecular structures of 1 (top panel) and 2 (bottom panel).

It has been previously reported that neutral complexes of the empirical formula $CuX(CNR)_2$ (X = any halogen) exhibit different structural types; in particular, in the solid-state XRD structures, they exist in the monomeric ($[CuCl(CNBu^{1})_{2}]^{31}$) or dimeric ($[Cu_2(\mu-X)_2(CNAr)_4]^{32-34}$ or $[Cu(\mu-I)(1,8-diisocyano-p-menthane)]_2^{35}$) forms. The coordination polymers of the 2-type were unknown before this study.

Complexes 1 and 2 were then cocrystallized with I_2 at different molar ratios (from 1:1 to 1:4) between the reactants. Depending on complex: I_2 molar ratios, we isolated and then studied various crystals by XRD, whose structures reflect a

gradual accumulation of iodine in the copper system. In particular, in the case of 1, we isolated cocrystals [$(Cu_2(\mu I)_2(CNXyI)_4)\cdot I_2$]·[$Cu_2(\mu_{1,1}-I_3)_2(CNXyI)_4$]₂ ([$1\cdot I_2$]·[3]₂, Cu:I ratio 3:8) and then the iodine adduct [$Cu_2(\mu_{1,3}-I_3)_2(CNXyI)_4$]. 2 I_2 (5·2 I_2 ; Cu:I ratio 1:5) (Scheme 1) and also, in the case of



2, a mixture of the isomeric 4^{A} and 4^{B} complexes $[\text{Cu}(\mu_{1,1}-I_3)(\text{CNC}_6\text{H}_3\text{-}2\text{-}\text{Cl}\text{-}6\text{-}\text{Me})_2]_2$ (in approximately equal amounts; Cu:I ratio: 1:3) and then $[\text{Cu}(\mu_{1,3}\text{-}\text{I}_3)(\text{CNC}_6\text{H}_3\text{-}2\text{-}\text{Cl}\text{-}6\text{-}\text{Me})_2]_{n'}n_2I_2$ ($6^{\cdot 1}/_2I_2$; Cu:I ratio: 1:4) (Scheme 2).





Complex $5.2I_2$ (for detailed analysis of its structure, see Section 2.3.1) exhibits the highest iodine content among the studied cocrystals. Notably, a further increase of the complex: I_2 ratio did not lead to other species having a higher iodine content.

The structure of $[1 \cdot I_2] \cdot [3]_2$ is built up by complex 1 which is linked with the bridging iodide $1 \cdot I_2$ and the triiodide 3 complexes featuring double the end-on triiodide bridging motif (Figure 3, top). Cocrystals $5 \cdot 2I_2$ are assembled by chains of I_2 and a binuclear 8-membered metallacycle with two end-to-end bridging triiodides. In the system $2/I_2$ (Scheme 2), a gradual increase in the amount of I_2 leads to a conversion of polymeric *catena*-complex 2 to two types of structures (4^A and 4^B). These structures featuring binuclear complexes are linked by the endon triiodide bridge (Figure 3, bottom). A subsequent increase in the amount of iodine leads to polymeric *catena*-complex 6 bearing end-to-end triiodide bridging ligands, whose chains are linked by HaB with I_2 to accomplish the resulting 3D structure of $6 \cdot \frac{1}{_2}I_2$.

In the case of XylNC, the inorganic structure in the corresponding solid-state structure was repeatedly reproduced. To get more examples of the 8-membered coordination cycles, we attempted to expand the reaction to other isocyanides. However, our manifold attempts to prepare similar chair-like inorganic structures using the isocyanides 2,4,6-Me₃C₆H₂NC and 2,6-Cl₂C₆H₃NC failed: we conducted these crystallizations using 2, 4, 6, and 8 iodine equivalents in CH₂Cl₂, CHCl₃, and $C_2H_4Cl_2$ at +20, + 4, and -20 °C. All these reactions gave either weakly diffracting crystals $(2,4,6-Me_3C_6H_2NC)$ or amorphous solids $(2,6-Cl_2C_6H_3NC)$. All attempts to obtain structures similar to $5.2I_2$ based on the isocyanide 2-Cl-6-Me-C₆H₃NC, led to a completely different type of supramolecular organization, namely to the coordination polymer $6^{1/2}I_{2}$ which does not exhibit the $Cu_2(\mu_{1,3}-I_3)_2$ core in the chair conformation. This result is probably explained by the collective action of various noncovalent forces, for example, the action of HaB including a Cl atom from the 2-Cl-6-Me- C_6H_3 moiety and an I atom of the triiodide (Figure S12).

2.3. Solid-State Structures of $5 \cdot 2I_2$ and $6 \cdot 1/2I_2$. 2.3.1. Structure of $5 \cdot 2I_2$. The crystal structure of the adduct $[Cu_2(\mu_{1,3}-I_3)_2(CNXyI)_4] \cdot 2I_2$ ($5 \cdot 2I_2$) is composed of binuclear complex 5 and molecular iodine (Figure 4). The copper ions demonstrate distorted tetrahedral geometries with the angles in the range of $97.06(2) - 144.4(2)^\circ$ and the geometry index $\tau'_4 = 0.65$.³⁶ The latter value reflects the geometry of the coordination center (0 for square planar and 1 for tetrahedral); the deviation from 1 for the ideal tetrahedral geometry is probably caused by the repulsion between two bulky isocyanide ligands and/or the effect of the proximity of the iodine molecule to the copper atom and two isocyanide ligands (see discussion later).

The Cu–I distances (2.7810(7) and 2.7991(6) Å) are slightly longer than the typical Cu^I–I bond length (2.563(77) Å)³⁹ and longer than the Cu^I–I distance (2.6976(18) Å) at the four-coordinated copper(I) ion (CSD refcode: RIQSUI).²¹ In adduct 5.2I₂, complex 5, bearing the $\mu_2(I^1,I^3)$ -I₃ ligands, exhibits the I–I bond lengths 11–I2 2.9053(4) and I2–I3 2.9014(4) Å, which are nearly the same within 3 σ , and this indicates that the bridging triiodide is almost symmetric. This type of I₃⁻ coordination is rather rare and only one structure of a linear polymeric Cu^I complex bearing the bridged triiodide was retrieved from the CSD, namely *catena*-([Cu($\mu_{1,3}$ -I₃){ μ_2 -(3,3',5,5'-tetramethyl-4,4'-bipyrazole)}]) (CSD refcode:



Figure 3. Structures of $[1 \cdot I_2]$ (top left) and [3] (top right) in the molecular structure of $[1 \cdot I_2] \cdot [3]_2$. The structures of the isomeric 4^B (bottom left) and 4^A (bottom right) complexes.

HUQDII⁴⁰). Other examples of the $\mu_{1,3}$ -triiodide moieties are represented by the structures of *catena*-([Cp*₂Cr₂(μ -Cl)(μ -I)₂($\mu_{1,3}$ -I₃)]) (KAJZIE⁴¹), *catena*-({Me₂S}₂[Pb₅(μ -I)₁₁($\mu_{1,3}$ -I₃)]·2I₂) (KOFZIR⁴²), *catena*-(K(19-crown-6)($\mu_{1,3}$ -I₃)) (TU-PSIG01⁴³), and *catena*-(Cs[Ni{3-MeOC₆H₃(2-O)(CH=N)}₂(CH₂)₃]($\mu_{1,3}$ -I₃)) (XEDCEO⁴⁴).

Complexes featuring the I_3^- -based 8-membered cycle, $[M_2(\mu_{1,3}-I_3)_2]$, have never been reported, and 5 represents a novel supramolecular motif—the double (triiodide)-bridging moiety linking two metal centers. However, cyclic complexes bearing linear three-center bridging ligands are rather abundant, e.g., copper(I- and II) complexes of this type with N₃⁻, SCN⁻, OCN⁻, and ArNCN⁻ ligands are, as verified by the CSD search, represented by 225 structures.

Bond distance in the iodine molecule (2.7334(5) Å) is typical for the solid I₂ (2.720(8) Å).⁴⁵ In the adduct, molecular

iodine and the triiodide ligand are assembled in infinite chains by HaB (Table 1 and Figure 4). These chains include the 10membered cyclic noncovalent motif $\{I_3 - I_2 \cdot I_3 - I_2\}$, which are assembled to give extended architectures via the copper(I) site, which is mutual for each I_3^- ligands. The occurrence of the cyclic HaB-based motif is rather typical for halogen compounds; for example, different conformations of such HaB-based cycles were recently observed.⁴⁶ The neighboring chains are connected via $\pi - \pi$ stacking interactions between the Xyl rings (interplane distances range from 3.435(5) to 3.520(6) Å). In addition, I₂ forms short contact with Cu (I5-Cu1 and I4-Cu1 distances are 4.0900(6) and 4.0059(7) Å, respectively; I–I_{bond} to Cu distance is 3.8084(6) Å; Figure S9), which can be attributed to semicoordination bonding.⁹ The CSD search for Cu...(I,I) contacts occurred between a Cu atom and I₂ (for Cu-I separations smaller than or equal to

Article

Figure 4. Molecular structure of adduct $5 \cdot 2I_2$ (I_2 molecule is omitted for simplicity; top panel) and supramolecular assembly based on I–I···I–Cu HaBs (bottom panel).

of 5•2L
(

contact	distances (Å) $(Nc)^a$	angles (deg)	comments
15…12	I5…I2 3.5193(5) (0.89 and 0.86)	I4—I5…I2 176.58(2)	type II contact
		I5…I2—I3 86.22(1)	
I4…I1	I4…I1 3.4347(5) (0.87 and 0.84)	I5–I4…I1 177.02(2)	type II contact
		I4…I1–I3 88.41(1)	
Cu…(I4,I5)	Cu1…I4 4.0060(7) (1.19 and 0.91)	I5–I4…Cu1 71.933(17)	semicoordination
	Cu1…I5 4.0899(6) (1.21 and 0.93)	I4–I5…Cu1 68.619(13)	
Xyl…Xyl	C16…C7 3.440(6) (1.01 and 0.97)		$\pi-\pi$ stacking
	C12…C3 3.520(6) (1.04 and 0.99)		
Xyl…Xyl	C7…C3 3.435(6) (1.01 and 0.97)		$\pi-\pi$ stacking
Xyl…Xyl	C16…C12 3.488(6) (1.03 and 0.99)		$\pi-\pi$ stacking

^{*a*}Hereinafter, Nc is the normalized contact distance, Nc = d/Bondi³⁷ \sum_{vdW} or d/Alvarez \sum_{vdW} , where Bondi \sum_{vdW} I + I 3.96; \sum_{vdW} Cu + I 3.38; \sum_{vdW} C + C 3.40 Å; Alvarez³⁸ \sum_{vdW} I + I 4.08; \sum_{vdW} Cu + I 4.42; and \sum_{vdW} C + C 3.54 Å. Alvarez \sum_{vdW} (Cu,I) = 4.42 Å), failing to reveal relevant structures. Search for Cu…I₂ two-center contacts gave three structures exhibiting short Cu…I(I₂) separations, namely MUPCOY (4.373 Å), TITTAU (3.865 Å), and VAMHOK (4.314 Å); all these structures are adducts that occurred between a copper(I) complex and I₂.

In the fragment $(XyINC)_2Cu\cdots I_2$, the $C_{isocyanide}\cdots(I,I)$ distances (3.830(5), 3.902(5), 4.064(4), and 3.985(5) Å) are greater than those of Bondi $\sum_{vdW}\!C$ + I 3.68 Å and Alvarez \sum_{vdW} C + I 3.8 Å; I–I_{bond} to C_{isocyanide} atom distances are $\overline{3.783(5)}$ and 3.615(5) Å. Comparison of these values gives a hint that weak C…(I,I) contacts, stabilizing the (XylNC)₂Cu… I₂ structural motif, may be realized in the studied system. This hypothesis is complementary to the results of our previous studies and all results together indicate nucleophilic-electrophilic dualism of iodine sites toward noncovalent linkages.^{11,47} We previously observed an unusual HaB in $[CuI(CNXyl)_3]$. CHX_3 (X = Br, I) systems between the halogen atoms of a haloalkane and two C atoms of the two isocyanide ligands (Figure 5). Now, we observed that molecular iodine functions as an electron donor (via its electron belt) toward an integrated electrophile, which includes copper(I) (which acts as a Lewis acid) and C-based π -holes located at two coordinated isocyano groups (for more details, see Section

Figure 5. Semicoordination (this work) and HaB^{11} in cocrystals of (RNC)Cu¹ species with iodine (bromine) derivatives.

2.4). Similar intermolecular C_{CN} ...I contacts were previously observed by some of us in (isocyanide)Pd^{II} complexes bearing an organoiodine functionality.⁴⁷

Each iodine molecule in the structure of $5 \cdot 2I_2$ is surrounded by three molecules of 5 (Figure S10). Two molecules of 5 form two I···I HaBs with I₂, while the third complex forms the Cu··· η^2 -I₂ semicoordination bond (Figure 5, left panel). These contacts can be treated as cooperative; in the former two structures, I₂ functions as an electron acceptor, whereas in the third, it acts as an electron donor.

2.3.2. Structure of $6 \cdot \frac{1}{2}I_2$. The structure of $[Cu(\mu - I_3)(CNC_6H_3-2-Cl-6-Me)_2]_n \cdot \frac{n}{2}I_2$ ($6 \cdot \frac{1}{2}I_2$) demonstrates disordering of the 2-Cl-6-MeC_6H_3 group in two positions. This uncertainty in the determination of positions of the Me and Cl substituents precludes accurate discussion of short contacts involving these atoms; however, other well-ordered fragments of the structure are worthy of detailed consideration.

The crystal structure of adduct $6 \cdot {}^{1}/{}_{2}I_{2}$ is built by coordination polymer **6** and molecular iodine (Figures 6 and S11). Polymeric complex **6** is composed of infinite 1D chains $\{(\mu_{1,3}\text{-}I_{3})\text{Cu}(\text{CNC}_{6}\text{H}_{3}\text{-}2\text{-}\text{Cl-}6\text{-}\text{Me})_{2}\}_{n}$. The copper atoms demonstrate distorted tetrahedral geometries with the angles in the range of 99.90(5)-140.5(4)° and the geometry index $\tau'_{4}^{36} = 0.70$, demonstrating the deviation from 1 required for the ideal tetrahedral geometry.

The Cu–I distances (2.7027(15), 2.7327(14) Å) are slightly longer than the typical Cu^I–I bond length (2.563(77) Å)³⁹ and comparable with those values for adduct **5**·2I₂. The $\mu_{1,3}$ -I₃ ligand exhibits slightly different I–I bond lengths (I1–I2 2.9585(8), I2–I3 2.8612(8) Å). Complex **6** in the adduct bears the $\mu_{1,3}$ -I₃ ligand. This type of I₃⁻ coordination is reported for only one copper complex, namely *catena*-([Cu($\mu_{1,3}$ -I₃){ μ_2 -(3,3',5,5'-tetramethyl-4,4'-bipyrazole)}]) (HUQDII⁴⁰); this structure also exhibits slightly different bond lengths for the $\mu_{1,3}$ -I₃ ligand (3.0398(9) and 2.8393(9) Å).

In the adduct, I_2 and the I_3^- ligand are linked by relatively short (and presumably strong) HaB, and due to this type contacts, 1D chains of **6** are assembled into two-dimensional (2D) layers via the I_2 bridges (Table 2 and Figure S11). Contacts arene_(-C_6H_3-2-Cl-6-Me)····Cl and intra- and interchain short separations Cl···I(I_3) were observed in the structure of **6**·¹/₂ I_2 (Figure S12). In view of the uncertainty in the determination of Cl/Me positions in the $-C_6H_3$ -2-Cl-6-Me group noticed above, we avoid consideration of the interactions involving the Cl atoms. Similar to **5**·2 I_2 , iodine in **6**·¹/₂ I_2 forms short contact with Cu (Table 2) and we

Figure 6. Fragment of the molecular structure of adduct $6 \cdot \frac{1}{2} I_{2i} I_{2}$ has been omitted for simplicity.

Table 2. Short Contacts in the Structure of $6 \cdot \frac{1}{2} I_2$

contact	distances (Å) (Nc)	angles (deg)	comments
I1…I25	I1…I25 3.4612(8) (0.87 and 0.84)	I25–I25…I1 176.79(4)	type II HaB
		I25…I1–I2 86.017(19)	
Cu…(I25,I25)	Cu4…I25 4.2329(15) (1.25 and 0.96)	I5–I4…Cu1 74.54(3)	semicoordination
	Cu4…I25 4.3810(14) (1.30 and 0.99)	I4–I5…Cu1 68.63(3)	

attributed this contact to the semicoordination bond.⁹ These contacts are slightly longer than those in $5.2I_2$.

Thus, the replacement of Xyl by 2-Cl-6-MeC₆H₃ in the system $[CuI(CNR)_2]_n/I_2$ leads to a change in the composition and structure of the iodine-containing cocrystals (Figure S13). Only with $[CuI(CNXyl)_2]_2$, it is possible to obtain a system whose supramolecular organization resembles the Hassel iodine-dioxane adduct, due to the occurrence of infinite HaB-based chains between I₂ and the dimeric cyclic complex 5. The replacement of a substituent R, in the case of $[CuI(CNC_6H_3-2-Cl-6-Me)_2]_n$, leads to crystallization of polymer 6 bearing bridged triiodide, which forms HaB with I₂. Probably, the introduction of the 2-Cl group in R, because of its involvement in various types of noncovalent interactions, leads to the implementation of the different structural motif.

2.4. Theoretical Considerations. To confirm the structure-determining nature of the I···I contacts as well as the presence of Cu···(I,I) interactions and determine the nature of all identified noncovalent interactions, we carried out appropriate theoretical calculations. Initially, the molecular electrostatic potential (MEP) surface of compound **5** was computed to investigate the most nucleophilic and electrophilic regions of the molecule and also to disclose the role of the copper(I) site in the assembly. Two different representations are shown in Figure 7, evidencing that the MEP minimum is located at the central I atom of the $\mu_{1,3}$ -I₃⁻ bridging ligand. The MEP value at the Cu-coordinated I atoms

Figure 7. MEP surfaces of 5 using a conventional colored mapping (a) and bicolor one (b); (c) MEP surface of I_2 . Values are in kcal/mol.

is slightly less negative (-26 kcal/mol). The MEP maximum (+22 kcal/mol) is located at the aromatic H atoms, followed by the methyl groups +14 kcal/mol. The MEP value is negative at the Cu atom along the bisector of the C-Cu-C angle (anticipating an electrostatic repulsion with the I₂ molecule in the orientation illustrated in Figure 5, left). To better visualize the negative/positive MEP in this part of the molecule, we represented in Figure 7b the MEP surface using a bicolor scheme (red for positive and blue for negative). The MEP is <0 kcal/mol at the Cu atom, neutral at the C atoms (~0 kcal/ mol), and >0 kcal/mol at the N atoms of the coordinated isocyano groups. The MEP surface of I_2 (Figure 7c) reveals its dominant electrophilic character with an intense σ -hole (+33) kcal/mol) and a quite modest MEP value at the negative belt (-4.3 kcal/mol). Such a small MEP value anticipates a small electrostatic repulsion between the Cu and the iodine atom of I₂ and that other forces can be more dominant. The nature of the $Cu \cdots I_2$ interaction is further analyzed below.

Initially, we computed a tetrameric assembly of compound 5 based on the I-I-I-Cu HaBs detailed above. The QTAIM/ NCIplot analysis of the assembly is represented in Figure 8a, showing that each HaB is characterized by a bond CP (small red sphere) and a bond path (solid line) interconnecting the I atoms. Moreover, bluish isosurfaces are also present coincident with the location of the bond CPs. The total formation energy of this assembly is -20.4 kcal/mol, thus evidencing the moderately strong nature of the HaBs, in line with the NCIplot analysis. We also estimated the energy of each HaB by using the equation proposed by Bartashevich and Tsirelson E_{int} = $-0.68 \times$ Gr, where Gr is the Lagrangian kinetic energy measured at the bond CP.⁴⁸ These values are given in red in Figure 8b, close to the bond CPs. The energies are -3.9 and -3.2 kcal/mol, corresponding to the I5…I2 and I4…I1 contacts, respectively, described above (Figure 4 and Table 1). By comparing the sum of the individual HaBs (-14.2 kcal/mol) with the interaction energy computed by using the supramolecular approach (-20.2 kcal/mol), it can be concluded that the G_r energy predictor underestimates the HaB contacts. This is likely because G_r was developed using O, N, S, and C as electron donors.

The analysis of the trimeric assembly with two symmetrically equivalent $Cu \cdot I_2$ interactions is shown in Figure 8b. Remarkably, each I_2 is connected to 5 by means of four CH…I H-bonds characterized by the corresponding bond CPs, bond paths, and green RDG isosurfaces, involving the methyl groups functioning as H-bond donors. This agrees well with the MEP surface analysis. Each I₂ molecule is also connected to one C atom of the isocyano group by means of two bond CPs and bond paths. Moreover, a large and green RDG isosurface is located between I₂ and the C–Cu–C core, suggesting that the interaction of the iodine's lone pairs (LP) includes the Cu atom and the two $C_{isocyano}$ atoms of the ligands (Figure 5). Further analysis of this interaction is given below. The formation energy of this assembly (-11.9 kcal/mol) is smaller than that of the HaB assembly, in line with the color of the isosurfaces.

The HaBs were further characterized using the electron localization function (ELF) method and natural bond orbital (NBO) analysis. The former is useful to locate the σ -holes and lone pairs, and the latter is used to analyze orbital donor-acceptor interactions (see refs 49,50 for details).

The ELF topographical 2D maps of the $\eta(\mathbf{r})$ function for the molecular plane defined by two I₂ molecules and two $\mu_{1,3}$ -I₃

Figure 8. QTAIM (BCPs in red and bond paths as orange lines) and NCIPlot (RDG = 0.5, $\rho_{cutoff} = 0.04$ au, -0.035 au $\leq (sign\lambda_2)*\rho \leq 0.035$ au) analyses of the HaB tetramer (a) and Cu,C₁C···I₂ trimer (b) of the 5·2I₂ cocrystal. Only intermolecular interactions are represented. The formation energies are also indicated. The individual HaB energies are indicated in red.

Figure 9. (a) Combined ELF and QTAIM projection of the tetrameric assembly of $5 \cdot I_2$. Bond CPs are represented as red dots with bond path as brown lines; (b) NBOs of the LP(I) $\rightarrow \sigma^*(I-I)$ in $5 \cdot I_2$. The total $E^{(2)}$ energy is also indicated.

Figure 10. NBOs of LP(I) $\rightarrow \pi^*(C \equiv N)$ (a) and LP(I) $\rightarrow LV(Cu)$ in 5·I₂ (b). The $E^{(2)}$ energies are also indicated.

ligands is shown in Figure 9a, where the bond CPs and bond paths characterizing the I···I HaBs are also represented. The inspection of the 2D map evince that the bond path that interconnects the I atoms crosses the σ -hole of the I₂ and the

lone pairs (LPs) at the Cu-coordinated I atom, typical for σ hole-based interactions. Regarding the NBO analysis, it shows very large orbital contribution, where LPs located at the Cucoordinated I atoms donate to the antibonding $\sigma^*(I-I)$

Finally, we studied the nature of the $Cu, C, C \cdots I_2$ interaction using the NBO method to verify the role of Cu. The result is shown in Figure 10, disclosing two types of charge transfer effects from I_2 to 5. Notably, no orbital contribution from 1 to I_2 has been found, thus confirming the electron donor nature of I₂ in this particular contact. The orbitals that participate in the charge transfer from the I_2 to the C \equiv N group are shown in Figure 10a, and it involves two LPs of both I atoms in I_2 to the π^* antibonding orbital of the C \equiv N group, namely LP(I) $\rightarrow \pi^*(C \equiv N)$. An equivalent charge transfer is observed to the other isocyano group. The associated stabilization energy for the LP(I) $\rightarrow \pi^*(C \equiv N)$ donor-acceptor orbital interactions is only 0.99 kcal/mol (1.98 kcal/mol in total for both isocyano groups), thus disclosing an I₂…C small contribution. A second type of charge transfer is also observed, and it involves the same orbitals at the I₂ molecule (LPs at both I atoms) and a lone valence orbital (LV) that is composed (>97%) by the empty 4s atomic orbital of Cu (Figure 10b). The concomitant $LP(I) \rightarrow LV(Cu)$ stabilization energy is 2.13 kcal/mol, thus suggesting a larger contribution of I_2 ...Cu than that of I_2 ...C (0.99 kcal/mol) in the Cu,C,C...I₂ interaction. Moreover, this result also confirms the role of Cu as an electron acceptor despite its negative MEP value, as shown in Figure 8b.

2.5. Conclusions. The example of $5 \cdot I_2$ demonstrates the existence of a novel supramolecular motif, the triiodide-based chair-like $Cu_2(\mu_{1,3}$ - $I_3)_2$ complex. These complexes are linked into an extended supramolecular structure based on HaB between the I_3^- ligands and the molecular iodine. The structure of $5 \cdot I_2$ resembles classical adducts of dioxane with molecular halogens, first described by Hassel (see the Introduction). The structure of $5 \cdot I_2$ can therefore be considered to be a coordination analogue of organic HaB-based dioxane adducts. As seen from the analysis of XRD data and the results of computational studies, the I···I HaBs in $5 \cdot I_2$ can be regarded as moderately strong noncovalent forces that determine the supramolecular organization of the cocrystals.

3. EXPERIMENTAL SECTION

3.1. Materials and Instrumentation. Solvents, CuI, I2, xylylisocyanide, and 2-chloro-6-methylphenyl isocyanide were obtained from commercial sources (Aldrich) and used as received, apart from CH₂Cl₂, which was purified by conventional distillation over CaCl₂. C, H, and N elemental analyses were carried out on an Euro EA 3028 HT CHNSO analyzer. The high-resolution mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization (ESI) source, and MeOH was used as the solvent. The instrument was operated in positive ion mode using a m/z range of 50–3000. The most intensive peak in the isotopic pattern is reported. Infrared spectra (4000-400 cm⁻¹) were recorded on a Shimadzu IRAffinity-1 FTIR spectrophotometer in KBr pellets. NMR spectra were recorded on Bruker AVANCE III 400 spectrometers in CDCl₃ at ambient temperature (at 400 and 100 MHz for ¹H and ¹³C NMR, respectively). Chemical shifts are given in δ -values (ppm) referenced to the residual signals of the undeuterated solvent (CHCl₃): δ 7.27 (¹H) and 77.0 (¹³C).

3.2. Synthetic Work and Characterization. 3.2.1. Synthesis of $[Cu(\mu-l)(CNR)_2]_n$ (n = 2, R = Xyl; $n = \infty$, $R = C_6H_3$ -2-Cl-6-Me). An isocyanide (0.68 mmol) was added to a suspension of CuI (65 mg, 0.34 mmol) in MeCN (20 mL), whereupon the reaction mixture was stirred for 40 min at 20 °C. The resulting homogenous solution (for xylylisocyanide) or suspension (for 2-chloro-6-methylphenyl isocyanide) was evaporated under a reduced pressure (20 mbar) at room

temperature (RT) to dryness, and the colorless residue was washed with Et_2O (two 2 mL portions) and then dried in air at room temperature.

The yield of $[Cu(\mu-I)(CNXyl)_2]_2$ (1) is 102 mg, 92%. Colorless solid. Calcd for $C_{36}H_{36}N_4Cu_2I_2$: C 47.75, H 4.01, N 6.19; Found: C 47.81, H 4.11, N 6.02. ESI HRMS⁺ (MeOH, m/z): 325.0757 ($[Cu(CNXyl)_2]^+$, calcd. 325.0761). FTIR, ν_{max} (KBr, cm⁻¹): 2142 s $\nu(C\equiv N)$. ¹H NMR (CDCl₃, δ): 2.44 (s, 6H, CH₃), 7.06 (d, ³J_{H,H} = 7.6 Hz, 2H, *m*-H from xylyl), 7.18 (t, ³J_{H,H} = 7.6 Hz, 1H, *p*-H from xylyl). ¹³C{¹H} NMR (CDCl₃, δ): 18.74 (CH₃), 125.84 (*ipso*-C from xylyl), 127.71 (*m*-C from xylyl), 129.14 (*o*-C from xylyl), 135.50 (*p*-C from xylyl), 150.83 (C_{isocranide}).

The yield of $[Cu(\mu-I)(CNC_6H_3-2-Cl-6-Me)_2]_n$ (2) is 113 mg, 91%. Colorless solid. Calcd for $C_{16}H_{12}N_2Cl_2CuI$: C 38.77, H 2.85, N 5.65; Found: C 38.34, H 2.96, N 5.51. ESI HRMS⁺ (MeOH, *m/z*): 364.9679 ($[Cu(CNC_6H_3-2-Cl-6-Me)_2]^+$, calcd. 364.9668). FTIR, ν_{max} (KBr, cm⁻¹): 2133 s $\nu(C\equivN)$. ¹H NMR (CDCl₃, δ): 2.55 (s, 3H, CH₃), 7.19 (d, ³J_{H,H} = 7.5 Hz, 2H), 7.25–7.32 (m, 2H). ¹³C{¹H} NMR (CDCl₃, δ): 19.38 (CH₃), 127.48 (CH from aryl), 128.82 (CH from aryl), 130.23 (CH from aryl), 132.26 (C from aryl), 138.43 (C from aryl); the C_{isocyanide} and C_{ipso} resonances were not detected. **3.3. Cocrystal Growth for the XRD Study.** Colorless crystals of

3.3. Cocrystal Growth for the XRD Study. Colorless crystals of 1 and 2 were obtained by slow evaporation of their CH_2Cl_2 solution at RT. The dark-brown crystals of $[1 \cdot I_2] \cdot [3]_2$, 4^A , and 4^B were obtained by dissolution of a mixture of 1 or 2 and I_2 (molar ratio 1:2) in CH_2Cl_2 at 20 °C followed by slow evaporation of this solution at room temperature for 3 days. The dark-brown crystals of $5 \cdot 2I_2$ and $6 \cdot 1/_2I_2$ were obtained analogously to those of $[1 \cdot I_2] \cdot [3]_2$, 4^A , and 4^B but at 1:5 molar ratio between 1 (or 2) and I_2 .

3.4. X-ray Structure Determinations. Suitable single crystals were selected and mounted on a MiTeGen tip via a crystallographic oil. Data were collected using an Xcalibur, Eos diffractometer (monochromated Mo K α radiation, $\lambda = 0.71073$ Å) at 100(2) K. In each case, the structure was solved with the ShelXT⁵¹ structure solution program using Intrinsic Phasing and refined with the refinement package incorporated in the OLEX2 program ShelXL⁵ package⁵² using least squares minimization. Empirical absorption correction was applied in the CrysAlisPro⁵³ program complex using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. Both isocyanide ligands in the asymmetric unit of $6 \cdot \frac{1}{2} I_2$ are disordered over two places with the superposition of the Cl and Me substituents. The refined population ratios for these functional groups are 9:11 and 2:3. The modeling of disorder was performed with the restraints imposed on the C-Cl and C-Me bond lengths and the constraints for atomic displacement parameters of equivalent non-hydrogen atoms from two parts.

The crystal data, data collection parameters, and structure refinement data are listed in Table S1. CCDC 2241005–2241006 and 2284665–2284669 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

3.5. Computational Details. The calculations reported herein were performed using the Turbomole 7.2 program.⁵⁴ The crystallographic coordinates were used for the calculations of the supramolecular assemblies. We used the crystallographic coordinates for the assemblies because we are interested in evaluating the interactions as they stood in the solid state. The level of theory used for the calculations was PBE0⁵⁵-D3⁵⁶/def2-TZVP.^{57,58} For iodine, this basis set includes effective core potentials (ECP) and takes into consideration relativistic effects for the inner electrons.⁵⁷ The formation energies of the assemblies were calculated by subtracting the electronic energy of the assemblies from the total electronic energy of the corresponding monomers. The MEP surface plots were generated using the wave function obtained at the same level of theory and the 0.001 au isosurface to simulate the van der Waals envelope. The topological analysis of the electron density was carried out according to the method of quantum theory of atoms in molecules (QTAIM) proposed by Bader⁵⁹ and the reduced density gradient (RDG) isosurfaces (NCIplot)⁶⁰ and represented using the VMD program.⁶¹ The electron localization function (ELF)⁴⁹ analysis

was performed using the MultiWFN program⁶² at the PB86-D3/def2-TZVP level of theory. The NBO analysis⁵⁰ was performed using the same level of theory and the NBO7.0 program.⁶³

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c02990.

NMR, FTIR, and ESI HRMS⁺ spectra, X-ray diffraction data, and schematic view of two structures (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Mikhail A. Kinzhalov Saint Petersburg State University, Saint Petersburg 199034, Russian Federation; Research School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University, Tomsk 634050, Russian Federation; orcid.org/0000-0001-5055-1212; Email: m.kinzhalov@ spbu.ru
- Nadezhda A. Bokach Saint Petersburg State University, Saint Petersburg 199034, Russian Federation; Research School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University, Tomsk 634050, Russian Federation; orcid.org/0000-0001-8692-9627; Email: n.bokach@ spbu.ru

Authors

- **Ekaterina I. Kinzhalova** Saint Petersburg State University, Saint Petersburg 199034, Russian Federation
- Valentina A. Karnoukhova A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 119991, Russian Federation
- Ivan V. Ananyev N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 119991, Russian Federation; Occid.org/0000-0001-6867-7534
- Rosa M. Gomila Department of Chemistry, Universitat de les Illes Balears, Palma de Mallorca 07122 Baleares, Spain; orcid.org/0000-0002-0827-8504
- Antonio Frontera Department of Chemistry, Universitat de les Illes Balears, Palma de Mallorca 07122 Baleares, Spain; orcid.org/0000-0001-7840-2139
- Vadim Yu. Kukushkin Saint Petersburg State University, Saint Petersburg 199034, Russian Federation; Laboratory of Crystal Engineering of Functional Materials, South Ural State University, Chelyabinsk 454080, Russian Federation;
 orcid.org/0000-0002-2253-085X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.3c02990

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The support of the Russian Science Foundation (Project 22-13-00078; synthesis and crystal engineering) and the Ministry of Science and Higher Education of the Russian Federation in the framework of the "Mega-grant project" (no. 075-15-2021-585; XRD studies) is gratefully acknowledged. A.F. is grateful to Project PID2020-115637GB-I00, funded by Ministerio de Ciencia e Innovación of Spain MCIN/AEI/10.13039/ 501100011033 (theoretical studies). A.F. is grateful to the Alexander von Humboldt Foundation for the J. C. Mutis Award. Physicochemical studies were performed at the Center for Magnetic Resonance, the Center for Chemical Analysis and Materials Research, the Center for XRD Studies, the Center for Diagnostics of Functional Materials for Medicine, and the Center for Thermogravimetric and Calorimetric Research Methods (all belonging to Saint Petersburg State University). The authors thank Dr. O.V. Khoroshilova for XRD data collection.

REFERENCES

(1) Alkorta, I.; Elguero, J.; Frontera, A. Not Only Hydrogen Bonds: Other Noncovalent Interactions. *Crystals* **2020**, *10* (3), 180.

(2) Cornaton, Y.; Djukic, J.-P. Noncovalent Interactions in Organometallic Chemistry: From Cohesion to Reactivity, a New Chapter. *Acc. Chem. Res.* **2021**, *54* (20), 3828–3840.

(3) Frontera, A.; Bauzá, A. On the Importance of σ -Hole Interactions in Crystal Structures. *Crystals* **2021**, *11* (10), 1205.

(4) Desiraju, 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.

(5) Hassel, O. Structural Aspects of Interatomic Charge-Transfer Bonding. *Science* **1970**, *170* (3957), 497–502.

(6) Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* **2016**, *116* (4), 2478–2601.

(7) Halogen Bonding: Fundamentals and Applications; Metrangolo, P.; Resnati, G., Eds.; Springer: Berlin, Heidelberg, 2008; Vol. XII, p 221.

(8) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. Halogen Bonding Based Recognition Processes: A World Parallel to Hydrogen Bonding. Acc. Chem. Res. 2005, 38 (5), 386–395.

(9) Bikbaeva, Z. M.; Ivanov, D. M.; Novikov, A. S.; Ananyev, I. V.; Bokach, N. A.; Kukushkin, V. Y. Electrophilic-Nucleophilic Dualism of Nickel(II) toward Ni center dot center dot center dot l Noncovalent Interactions: Semicoordination of Iodine Centers via Electron Belt and Halogen Bonding via sigma-Hole. *Inorg. Chem.* **2017**, 56 (21), 13562–13578.

(10) Efimenko, Z. M.; Novikov, A. S.; Ivanov, D. M.; Piskunov, A. V.; Vereshchagin, A. A.; Levin, O. V.; Bokach, N. A.; Kukushkin, V. Y. The (Dioximate)NiII/12 System: Ligand Oxidation and Binding Modes of Triiodide Species. *Inorg. Chem.* **2020**, *59* (4), 2316–2327.

(11) Kinzhalov, M. A.; Ivanov, D. M.; Melekhova, A. A.; Bokach, N. A.; Gomila, R. M.; Frontera, A.; Kukushkin, V. Y. Chameleonic metalbound isocyanides: a π -donating CuI-center imparts nucleophilicity to the isocyanide carbon toward halogen bonding. *Inorg. Chem. Front.* **2022**, 9 (8), 1655–1665.

(12) Svensson, P. H.; Kloo, L. Synthesis, Structure, and Bonding in Polyiodide and Metal Iodide-Iodine Systems. *Chem. Rev.* 2003, 103 (5), 1649–1684.

(13) Haller, H.; Riedel, S. Recent Discoveries of Polyhalogen Anions—from Bromine to Fluorine. Z. Anorg. Allg. Chem. 2014, 640 (7), 1281–1291.

(14) Kloo, L. Catenated Compounds-Group 17-Polyhalides. In *Comprehensive Inorganic Chemistry II*, 2nd ed.; Reedijk, J.; Poeppelmeier, K., Eds.; Elsevier: Amsterdam, 2013; pp 233–249.

(15) Adonin, S. A.; Sokolov, M. N.; Fedin, V. P. Polyhalide-bonded metal complexes: Structural diversity in an eclectic class of compounds. *Coord. Chem. Rev.* **2018**, 367, 1–17.

(16) Korobeynikov, N. A.; Usoltsev, A. N.; Abramov, P. A.; Komarov, V. Y.; Sokolov, M. N.; Adonin, S. A. Trimethylammonium Sn(IV) and Pb(IV) Chlorometalate Complexes with Incorporated Dichlorine. *Inorganics* **2023**, *11* (1), 25.

(17) Korobeynikov, N. A.; Usoltsev, A. N.; Kolesov, B. A.; Abramov, P. A.; Plyusnin, P. E.; Sokolov, M. N.; Adonin, S. A. Dichlorinecontaining chlorobismuthate(iii) supramolecular hybrid: structure and experimental studies of stability. *CrystEngComm* **2022**, *24* (17), 3150–3152. (18) Usoltsev, A. N.; Korobeynikov, N. A.; Kolesov, B. A.; Novikov, A. S.; Samsonenko, D. G.; Fedin, V. P.; Sokolov, M. N.; Adonin, S. A. Rule, Not Exclusion: Formation of Dichlorine-Containing Supramolecular Complexes with Chlorometalates(IV). *Inorg. Chem.* **2021**, 60 (6), 4171–4177.

(19) Usoltsev, A. N.; Adonin, S. A.; Kolesov, B. A.; Novikov, A. S.; Fedin, V. P.; Sokolov, M. N. Opening the Third Century of Polyhalide Chemistry: Thermally Stable Complex with "Trapped" Dichlorine. *Chem. - Eur. J.* **2020**, *26* (61), 13776–13778.

(20) Usoltsev, A. N.; Korobeynikov, N. A.; Kolesov, B. A.; Novikov, A. S.; Abramov, P. A.; Sokolov, M. N.; Adonin, S. A. Oxochloroselenate(IV) with Incorporated {Cl2}: The Case of Strong Cl…Cl Halogen Bonding. *Chem. - Eur. J.* **2021**, *27* (36), 9292–9294. (21) Hu, J.; Zhou, J.; Cao, S. An unusual cuprous iodide polymer incorporating I-, I2 and I3- structural units. *Dalton Trans.* **2018**, *47* (48), 17216–17220.

(22) Zhao, S.-B.; Wang, R.-Y.; Wang, S. Dinuclear Cu(I) Complexes of 1,2,4,5-Tetra(7-azaindolyl)benzene: Persistent 3-Coordinate Geometry, Luminescence, and Reactivity. *Inorg. Chem.* **2006**, *45* (15), 5830–5840.

(23) Sultana, R.; Lobana, T. S.; Castineiras, A. Chemistry of heterocyclic-2-thiones: in situ generated 1-(4,5-dihydro-3-alkyl-imidazolidin-2-yl)-3-alkyl-imidazolidine-2-thione and triiodide form novel mixed valent CuI–II/CuII complexes. *RSC Adv.* **2015**, *5* (122), 100579–100588.

(24) Pan, Z.; Xu, J.; Zheng, H.; Huang, K.; Li, Y.; Guo, Z.; Batten, S. R. Three New Heterothiometallic Cluster Polymers with Fascinating Topologies. *Inorg. Chem.* **2009**, *48* (13), 5772–5778.

(25) He, J.; Duan, J.; Shi, H.; Huang, J.; Huang, J.; Yu, L.; Zeller, M.; Hunter, A. D.; Xu, Z. Immobilization of Volatile and Corrosive Iodine Monochloride (ICl) and I2 Reagents in a Stable Metal–Organic Framework. *Inorg. Chem.* **2014**, *53* (13), 6837–6843.

(26) Boyarskiy, V. P.; Bokach, N. A.; Luzyanin, K. V.; Kukushkin, V. Y. Metal-Mediated and Metal-Catalyzed Reactions of Isocyanides. *Chem. Rev.* **2015**, *115* (7), 2698–2779.

(27) Kuznetsov, M. L.; Pombeiro, A. J. L. Theoretical study of redox induced isomerizations, structure and bonding of nitrile, isocyanide and carbonyl complexes of rhenium. *Dalton Trans.* **2003**, No. 4, 738–747.

(28) Kinzhalov, M. A.; Ivanov, D. M.; Shishkina, A. V.; Melekhova, A. A.; Suslonov, V. V.; Frontera, A.; Kukushkin, V. Y.; Bokach, N. A. Halogen Bonding between Metal-bound I3- and Unbound I2: The Trapped I2…I3- Intermediate in the Controlled Assembly of Copper(I)-based Polyiodides. *Inorg. Chem. Front.* **2023**, *10*, 1522–1533.

(29) Katkova, S. A.; Mikherdov, A. S.; Kinzhalov, M. A.; Novikov, A. S.; Zolotarev, A. A.; Boyarskiy, V. P.; Kukushkin, V. Y. (Isocyano Group pi-Hole)…dz2-M-II Interactions of (Isocyanide) M-II Complexes, in which Positively Charged Metal Centers (d(8)-M = Pt, Pd) Act as Nucleophiles. *Chem. - Eur. J.* **2019**, *25* (36), 8590–8598.

(30) Kryukova, M. A.; Ivanov, D. M.; Kinzhalov, M. A.; Novikov, A. S.; Smirnov, A. S.; Bokach, N. A.; Kukushkin, V. Y. Four-Center Nodes: Supramolecular Synthons Based on Cyclic Halogen Bonding. *Chem. - Eur. J.* **2019**, *25* (60), 13671–13675.

(31) Bowmaker, G. A.; Hanna, J. V.; Hahn, F. E.; Lipton, A. S.; Oldham, C. E.; Skelton, B. W.; Smith, M. E.; White, A. H. Structural and spectroscopic studies of some copper(i) halide tert-butyl isocyanide adducts. *Dalton Trans.* **2008**, No. 13, 1710–1720.

(32) Willcocks, A. M.; Pugh, T.; Cosham, S. D.; Hamilton, J.; Sung, S. L.; Heil, T.; Chalker, P. R.; Williams, P. A.; Kociok-Kohn, G.; Johnson, A. L. Tailoring precursors for deposition: synthesis, structure, and thermal studies of cyclopentadienylcopper(i) iso-cyanide complexes. *Inorg. Chem.* **2015**, *54* (10), 4869–4881.

(33) Toth, A.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. Structurally diversified neutral copper(I) isocyanide complexes: mono- and binuclear complexes from the reaction of copper(I) halides with p-tolyl isocyanide. *J. Chem. Soc., Dalton Trans.* **1988**, No. 6, 1599–1605. (34) Benouazzane, M.; Coco, S.; Espinet, P.; Barberá, J. Binuclear Mesogenic Copper(I) Isocyanide Complexes with an Unusual Inorganic Core Formed by Two Tetrahedra Sharing an Edge. *Inorg. Chem.* **2002**, *41* (22), 5754–5759.

(35) Fortin, D.; Drouin, M.; Turcotte, M.; Harvey, P. D. Quasi-Unidimensional $\{[M(dmb)2]Y\}$ n Organometallic Polymers (M = Cu(I), Ag(I); dmb = 1,8-Diisocyano-p-menthane; Y = BF4-, PF6-, NO3-, ClO4-, CH3CO2-).1a Structural, Calorimetric, and Luminescence Properties. J. Am. Chem. Soc. **1997**, 119 (3), 531–541.

(36) Okuniewski, A.; Rosiak, D.; Chojnacki, J.; Becker, B. Coordination polymers and molecular structures among complexes of mercury(II) halides with selected 1-benzoylthioureas. *Polyhedron* **2015**, *90*, 47–57.

(37) Bondi, A. Van der Waals Volumes and Radii. J. Phys. Chem. A **1964**, 68 (3), 441–451.

(38) Alvarez, S. A cartography of the van der Waals territories. Dalton Trans. 2013, 42 (24), 8617-8636.

(39) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. Supplement. Tables of bond lengths determined by X-ray and neutron diffraction. Part 2. Organometallic compounds and co-ordination complexes of the d- and f-block metals. *J. Chem. Soc., Dalton Trans.* **1989**, No. 12, S1–S83.

(40) He, J.; Cao, P.; Wu, C.; Huang, J.; Huang, J.; He, Y.; Yu, L.; Zeller, M.; Hunter, A. D.; Xu, Z. Highly Polarizable Triiodide Anions (I3-) as Cross-Linkers for Coordination Polymers: Closing the Semiconductive Band Gap. *Inorg. Chem.* **2015**, *54* (13), 6087–6089.

(41) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. Chrom(III)und Chrom(IV)-Komplexe der π -Aromaten-Reihe: Präparative und strukturchemische Aspekte. *J. Organomet. Chem.* **1988**, 353 (3), 323– 336.

(42) Starkholm, A.; Kloo, L.; Svensson, P. H. Polyiodide Hybrid Perovskites: A Strategy To Convert Intrinsic 2D Systems into 3D Photovoltaic Materials. *ACS Appl. Energy Mater.* **2019**, 2 (1), 477– 485.

(43) Jones, P. G.; Dix, I. CCDC 692677: Experimental Crystal Structure Determination; University of Manchester, 2009.

(44) Cunningham, D.; McArdle, P.; Mitchell, M.; Ní Chonchubhair, N.; O'Gara, M.; Franceschi, F.; Floriani, C. Adduct Formation between Alkali Metal Ions and Divalent Metal Salicylaldimine Complexes Having Methoxy Substituents. A Structural Investigation. *Inorg. Chem.* **2000**, *39* (8), 1639–1649.

(45) Buontempo, U.; Di Cicco, A.; Filipponi, A.; Nardone, M.; Postorino, P. Determination of the I2 bond-length distribution in liquid, solid and solution, by extended x-ray absorption fine structure spectroscopy. J. Chem. Phys. **1997**, 107 (15), 5720–5726.

(46) Swathi Krishna, P. E.; Babu, H. C.; Nair, N. G.; Hariharan, M. Boat and Chair Shaped Hexahalogen Synthons. *Chem. - Asian J.* **2023**, *18* (6), No. e202201248.

(47) Mikherdov, A. S.; Katkova, S. A.; Novikov, A. S.; Efremova, M. M.; Reutskaya, E. Y.; Kinzhalov, M. A. (Isocyano group)…lone pair interactions involving coordinated isocyanides: experimental, theoretical and CSD studies. *CrystEngComm* **2020**, *22* (7), 1154–1159.

(48) Bartashevich, E. V.; Tsirelson, V. G. Interplay between noncovalent interactions in complexes and crystals with halogen bonds. *Russ. Chem. Rev.* 2014, 83 (12), 1181.

(49) Becke, A. D.; Edgecombe, K. E. A simple measure of electron localization in atomic and molecular systems. *J. Chem. Phys.* **1990**, 92 (9), 5397–5403.

(50) Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 7.0: New vistas in localized and delocalized chemical bonding theory. *J. Comput. Chem.* **2019**, 40 (25), 2234–2241.

(51) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64 (1), 112–122.

(52) 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. Crystallogr.* **2009**, *42* (2), 339–341.

(53) Agilent, C. CrysAlis PRO; Agilent Technologies Ltd: Yarnton, Oxfordshire, 2014.

(54) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic structure calculations on workstation computers: The program system turbomole. *Chem. Phys. Lett.* **1989**, *162* (3), 165–169.

(55) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, *110* (13), 6158–6170.

(56) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), No. 154104.

(57) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, 8 (9), 1057–1065.

(58) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, 7 (18), 3297–3305.

(59) Bader, R. F. W. A quantum theory of molecular structure and its applications. *Chem. Rev.* **1991**, *91* (5), 893–928.

(60) Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. NCIPLOT: A Program for Plotting Noncovalent Interaction Regions. *J. Chem. Theory Comput.* **2011**, 7 (3), 625–632.

(61) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* **1996**, *14* (1), 33–38.

(62) Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33 (5), 580–592.

(63) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Karafiloglou, P.; Landis, C. R.; Weinhold, F. *NBO* 7.0; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2018.