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FULL PAPER

Iodine(I) and Silver(I) Complexes of Benzoimidazole and Pyridylcarbazole Derivatives

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Abstract: The synthesis of iodine(I) complexes with either benzoimidazole or carbazole-derived sp^2 *N*-containing Lewis bases is described, as well as their corresponding silver(I) complexes. The addition of elemental iodine to the linear two-coordinate Ag(I) complexes produces iodine(I) complexes with a three-center four-electron (3c-4e) [N—I—N]$^+$ bond. The ^{1}H and ^{1}H-^{15}N HMBC NMR studies unambiguously confirm the formation of the complexes in all cases via the [N—Ag—N]$^+$ → [N—I—N]$^+$ cation exchange, with the ^{15}N NMR chemical shift change between 94 to 111 ppm when compared to the free ligand. The single crystal X-ray crystallographic studies on eight I$^+$ complexes revealed highly symmetrical [N—I—N]$^+$ bonds with I—N bond distances of 2.21 - 2.26 Å and N—I—N angles of 177 - 180°, whilst some of the corresponding Ag$^+$ complexes showed a clear deviation from linearity with N—Ag—N angles of ca. 150° and Ag—N bond distances of 2.09 - 2.18 Å.

Introduction

The basis of halogen bonding has been known for more than two centuries, and since then, it has played a major role in important achievements especially by R. S. Mulliken[1] and O. Hassel,[2] which earned them the Nobel prize in chemistry in 1966 and 1969, respectively. However, at the time, the results were not collectively understood, and it took roughly 30 years for it to gain its footing as a truly intriguing interaction in the field of supramolecular chemistry.[3] This relatively novel interaction was defined in 2013 to "*occur when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom (X) in a molecular entity and a nucleophilic region in another, or the same, molecular entity*", where X = Cl, Br, or I.[4,5] Although halogens are generally viewed as electronegative, since the 1990s it has been well established that strongly polarized halogen atoms manifest a positively charged electrostatic potential, a so-called σ-hole.[3,4] Alternatively, this phenomenon can be explained by the charge-transfer theory by Mulliken[6] or polar flattening.[7] Therefore, a halogen atom is capable of interacting with a nucleophilic site, *i.e.* a Lewis base.[4] Since its discovery, halogen bonding has begun to unearth its potential in the design and preparation of self-assembled systems, as well as in crystal engineering.[8–11] This all due to its tunability, strength, and high directionality, making it an essential addition to the 'modern chemist's toolbox'.[3,11]

In a classical halogen bond consisting of a covalent bond and a halogen bond (D—X···D), the halogen atom exists in a formal oxidation state of -1 (*e.g.* in alkyl halides).[12] When electron is removed from the halogen atom, it becomes a positively charged halogen(I) cation (X$^+$), which forms three-center four-electron (3c-4e) [N—X—N]$^+$ bonds, in which X$^+$ simultaneously interacts with two nucleophiles (Lewis bases, D) both contributing a lone pair to stabilize the interaction [D···X···D]$^+$.[12–16] When aromatic Lewis bases are involved, the interaction is further enhanced by efficient charge transfer from the halogen(I) cation to the nucleophilic sites.[12,17,18] These halogen(I) cations were first discovered in the 1960s and since then, they have found applications in form of Barluenga's reagent[19] in synthetic chemistry as iodinating agents for aromatic electrophilic substitutions and aromatic amines, yet can also be used as oxidizing agents.[20–25] The exceptional strength of 3c-4e halogen bonds in halogen(I) complexes has made these an interesting sub-class of halogen-bonded complexes, however, due to their inherent reactivity only a few tens of unique iodine(I) complexes have been reported to date in the solid-state.[13,26–34] There are no reported X-ray structures of iodine(I) complexes with bicyclic aromatic amines such as benzoimidazoles or quinolines. Herein, benzoimidazole and pyridylcarbazole derivatives were chosen to probe halogen bonding with polycyclic and larger XB acceptors leading to eight new [N—I—N]$^+$ halogen(I) (also known as *halonium*) and [N—Ag—N]$^+$ silver(I) complexes in the solid-state, along with compelling evidence of halogen(I) complex formation in solution.

Results and Discussion

The syntheses of compounds **1** – **4** and **6** – **7** (Scheme 1) followed previously reported methods,[35–37] whilst compound **5** was obtained commercially. The ligands were reacted with silver(I) salts ($AgPF_6$, $AgBF_4$, and $AgSbF_6$) in a 2:1 ratio to obtain the [N—Ag—N]$^+$ silver(I) complexes. The corresponding [N—I—N]$^+$ halogen(I) complexes were obtained through the [N—Ag—N]$^+$ → [N—I—N]$^+$ cation exchange reaction (Scheme 2) by the addition of elemental iodine (I_2) to a solution of the silver(I) complexes,[12,15,38] which concomitantly resulted in the immediate precipitation of AgI.

The conversion from the free ligand to the silver(I) and iodine(I) complexes was confirmed with ^{1}H NMR spectroscopy (Figures S1-S5 and Table S1) and ^{1}H-^{15}N HMBC correlation measurements (Figures S6-S10). Ideally, all NMR measurements would have been performed in a non-coordinating solvent such

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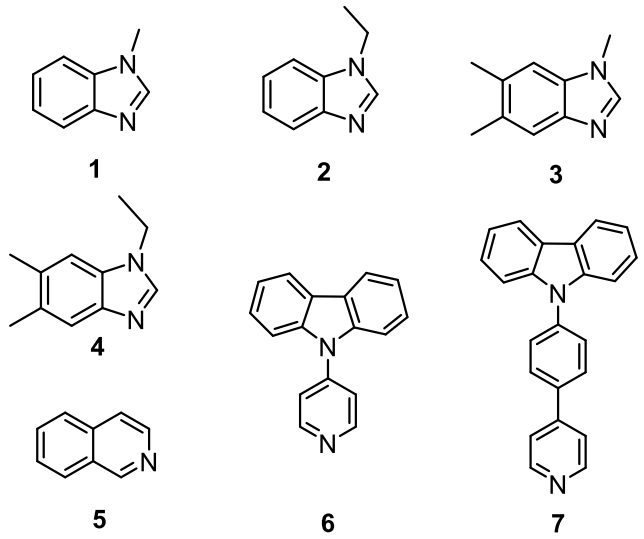
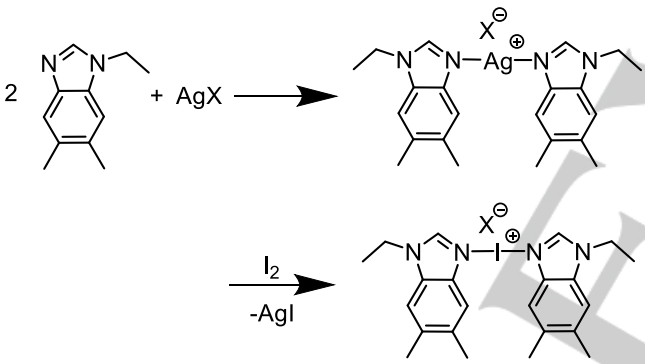
as CD_2Cl_2, but unfortunately, due to the solubility of either the ligand or the silver salt, all NMR measurements were necessarily



Scheme 1. Synthesized ligands **1** – **7** (compound **5** obtained commercially) used for the formation of the iodine(I) complexes.[35–37]



Scheme 2. Synthesis of the **[4—Ag—4]PF₆** silver(I) and **[4—I—4]PF₆** iodine(I) complexes via a cation exchange reaction.[12,15,38] All other complexes were prepared in an analogous fashion (where X = PF_6^-. BF_4^-, or SbF_6^-).

[12,15,38]performed in polar solvents, such as CD_3CN, acetone-d_6, or DMSO-d_6. The ^{1}H NMR analyses of the silver complexes **[L—Ag—L]PF₆** (exemplified in Figure 1) indicated a full conversion from the ligands to the silver(I) complexes and demonstrated significant complexation-induced changes in the chemical shifts. Changes in the chemical shifts when going from the free ligand to the silver(I) complex were found in the range of 0.02 - 0.47 ppm, with the greatest change being observed for **[3—Ag—3]PF₆** (Figure S3).

Measurements of the ligand and silver(I) salts proceeded straightforwardly, but for some of the ligands the solubility of the iodine(I) complex proved problematic. Since the synthesis comprises precipitation of AgI due to the cation exchange reaction, the poor solubility of the iodine(I) complexes could not be readily observed other than by the lower concentration indicated by the ^{1}H NMR spectra. Nevertheless, the ^{1}H NMR spectra were recorded for all of the iodine(I) complexes, except for **[7—I—7]**$^+$. Complexes from ligand **7** remained elusive, since the Ag^+ and I^+ complexes could not be solubilized, and therefore NMR analysis was not performed for these complexes. The comparison of the ^{1}H NMR spectra of the ligand **4**, the silver(I) complex **[4—Ag—4]PF₆**, and the iodine(I) complex **[4—I—4]PF₆** is shown in Figure 1. As expected, the cation exchange from the silver(I) to the iodine(I) results in a further downfield change in the chemical shifts of the bound ligand. Again, none of the silver(I) complex was observed in the spectrum for **[4—I—4]PF₆** (Figure 1), indicating a complete conversion. The changes in the chemical shifts in the ^{1}H NMR spectrum from the silver(I) complex to the iodine(I) complex are within the range of 0.13 - 0.59 ppm, making the total chemical shift change from ligand to iodine(I) complex between 0.36 - 1.06 ppm. The largest change in the chemical shift upon conversion from the ligand to the

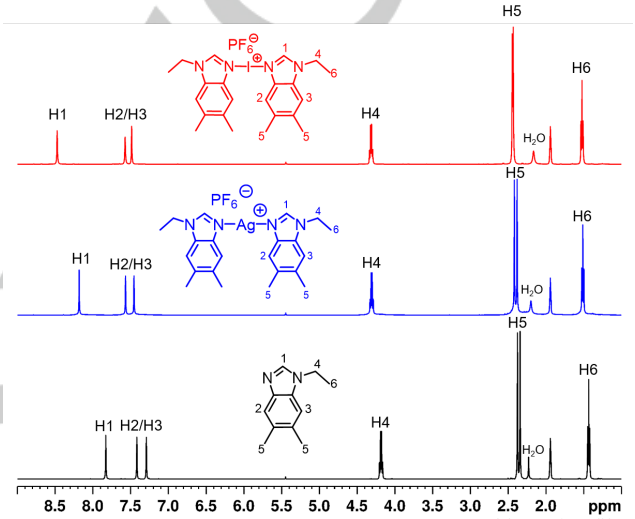


Figure 1. The comparison of the ^{1}H NMR spectra of ligand **4**, the silver(I) complex **[4—Ag—4]PF₆**, and the iodine(I) complex **[4—I—4]PF₆** (from bottom to top). All values are in ppm and referenced to CD_3CN (^{1}H) (500 MHz, 298 K).

iodine(I) complex was observed for ligand **3** (Figure S3), however, the poor solubility of **[3—I—3]PF₆** resulted in a broadened and less accurate spectrum.

The use of ^{1}H-^{15}N HMBC NMR spectroscopy provides a more powerful tool compared to the relatively small changes in the ^{1}H NMR spectra. The wide chemical shift range of the ^{15}N NMR and the direct involvement of the nitrogen nuclei in the complexation event render ^{15}N a convenient technique for monitoring the cation exchange reaction.[14,18,30,32,38,39] However, due to the fact that the ^{15}N nuclei is much less abundant in comparison to ^{1}H, not all the ^{1}H-^{15}N HMBC spectra could be obtained owing to the low solubility of several of the iodine(I) complexes. This is potentially made worse due to line broadening caused by an ongoing association-dissociation equilibrium, observed more prominently for weaker halogen-bond acceptors.[40] However, all three spectra of the complexation (ligand, silver(I), and iodine(I)) were obtained for several of the ligands (Figures S6-S10). The comparison of the ^{1}H-^{15}N HMBC correlation spectra of the ligand **4**, the silver complex **[4—Ag—4]PF₆**, and the iodine(I) complex **[4—I—4]PF₆** is shown in Figure 2. All ligands, except **5** (as predicted), provided two signals for the two nitrogen atoms in different environments. The sp^2-acceptor *N*-atom (N1) signal change was 44 ppm going from the ligand to the silver(I) complex

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[4—Ag—4]PF₆. Upon addition of the molecular iodine, an additional change of 50 ppm was observed for **[4—I—4]PF₆**, making it a total difference of 94 ppm (between the uncoordinated ligand and the iodine(I) complex). The largest change in the

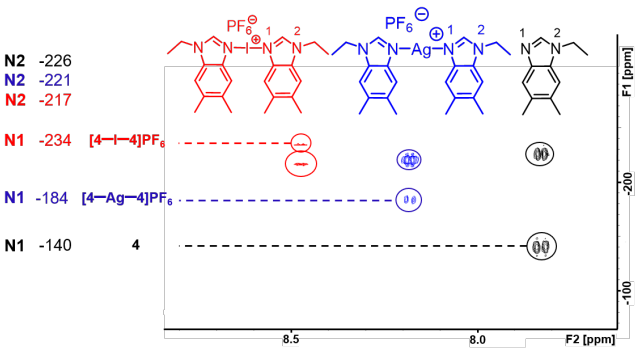

Figure 2. The comparison of the ^{1}H-^{15}N HMBC correlation spectra of the ligand **4**, the silver(I) complex **[4—Ag—4]PF₆**, and the iodine(I) complex **[4—I—4]PF₆**. All values are in ppm and referenced to CD_3CN (^{1}H) or CD_3NO_2 (^{15}N) (500 MHz, 298 K).

chemical shift from the ligand to the iodine(I) complex was observed for **[5—I—5]PF₆** (111 ppm, Figure S9).

Whilst the ^{15}N NMR resonances of the acceptor N1 are deshielded upon complexation, the inert N2 is shielded and experiences only minor changes in the chemical shift (9-10 ppm). Due to the low solubility of **[3—I—3]PF₆**, only the inert N2 resonance was observed, however the same trend was found in these chemical shift changes (Figure S8). The ^{1}H-^{15}N HMBC chemical shifts are summarized in Table 1.

Table 1. The ^{1}H-^{15}N HMBC chemical shifts of the N1 (top) and N2 (bottom) nuclei upon silver(I) and iodine(I) complexation for ligands **1** – **6** (where N1 is an acceptor for the silver(I) and iodine(I), and N2 is the non-coordinating nitrogen). All values reported in ppm.

Complex[a]	Ligand	[N—Ag—N]$^{+}$	[N—I—N]$^{+}$
[1—X—1]$^{+}$	-138.9 -238.3	-178.5 -233.1	-232.0 -228.5
[2—X—2]$^{+b}$	-138.4 -223.1	-180.7 -218.2	-232.2 -214.1
[3—X—3]$^{+b}$	-138.0 -239.1	-180.2 -235.0	- -229.7
[4—X—4]$^{+}$	-140.3 -225.9	-184.2 -220.6	-234.4 -216.6
[5—X—5]$^{+c}$	-70.1	-106.1	-181.9
[6—X—6]$^{+b}$	-67.7 -251.9	-124.8 -251.0	- -

[a] With PF_6^- counter-anion. [b] Poor solubility of the iodine(I) complex. [c] Only N1.

The solvent and counter-anion coordination to the silver(I) cation has previously been reported to affect the pyridine ^{15}N NMR coordination shifts.[12,30,41] Here, only $AgPF_6$ was used in the NMR analysis, and as a weakly coordinating anion, PF_6^- should not compete to coordinate to the silver(I). However, the CD_3CN is a coordinating solvent and interacts with the silver(I), decreasing its positive charge and, consequently, decreasing the charge transfer from the nitrogen atoms of the ligands to the silver(I) metal centers, resulting in smaller ^{15}N NMR coordination shifts. A significant change (48%) in the ^{15}N NMR resonance has previously been reported for the [*bis*(pyridine)silver(I)]$^{+}$ triflate complex upon solvent change from $CDCl_3$ to CD_3CN.[41] However, this should not be the case with the iodine(I) complexes due to the 3c-4e halogen bond, which forms only linear, two-coordinate [N—I—N]$^{+}$ species.

To further confirm the formation of the iodine(I) complexes, extensive efforts were made to crystallize and analyze the solid-state structures of these complexes. To date, only a limited number of X-ray structures of iodine(I) complexes have been reported due to their inherent reactivity as halogenating and oxidizing reagents.[23–25] The X-ray structures of ligands **3** – **4** and **6** – **7** (Figures S22, S26, S39, and S48), silver(I) complexes of all seven ligands, and the iodine(I) complexes of **1**, **2**, **4**, and **5** (Figures S13, S15, S20, S28, S34, S35, S36, and S37) were successfully obtained. As seen in the above NMR analysis, the iodine(I) complexes for **3**, **6**, and **7** were found to be problematic with regards to solubilizing them, even in the most polar solvents, rendering meaningful crystallization attempts moot.

The silver(I) complexes (Figures S11, S17, S18, S23, S27, S30, S32, S33, S40, S42, S44, S49) demonstrated Ag—N bond lengths between 2.086(3) - 2.177(2) Å (listed in Table S2), which is well within the previously reported values for similar structures.[30,33] Several silver(I) complexes were found to crystallize as dimers bonded through argentophilic closed-shell (d^{10}-d^{10}) interactions. The $Ag^{+}\cdots Ag^{+}$ argentophilic interactions were determined to be between 3.02 - 3.34 Å (Table S2) for the argentophilic dimers, yet longer interactions were also observed for two complexes **[5—Ag—5]PF₆** (d($Ag^{+}\cdots Ag^{+}$) = 3.81 Å, Figure S31) and **[6—Ag—6]PF₆** (d($Ag^{+}\cdots Ag^{+}$) = 3.61 Å, Figure S41). Figure 3 depicts the single crystal X-ray structure of **[7—Ag—7]PF₆** with coordinating acetonitrile and the argentophilic interactions between two **[7—Ag—7]$^{+}$** cations. The complex experiences a decisively short $Ag^{+}\cdots Ag^{+}$ interaction of 3.018(2) Å, well below the van der Waals radii of two Ag atoms (3.44 Å).[42] The strong $Ag^{+}\cdots Ag^{+}$ interaction causes torsion and applies strain to the ligand, but due to the inherent flexibility of **7**, close ligand-assisted $Ag^{+}\cdots Ag^{+}$ contact is possible, such as the perpendicular C—H···π (C37 to centroid = 3.6 Å) interactions.

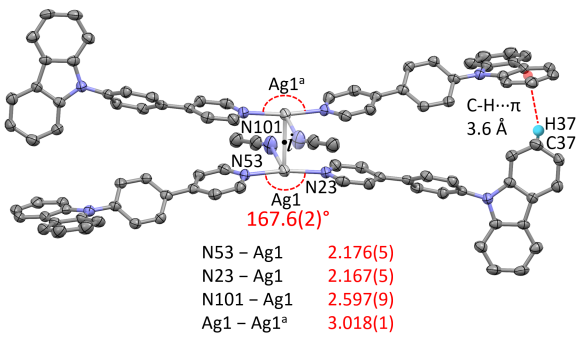

Figure 3. The X-ray structure of **[7—Ag—7]PF₆**, showing the argentophilic dimer observed in solid-state (counter-anions and hydrogen atoms omitted for clarity. Thermal displacement ellipsoids drawn at the 50% probability level; all lengths in Å). Symmetry operator: a = 1 – *x*, 1 – *y*, 1 – *z*.

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Silver(I) has a flexible coordination sphere and is able to accommodate multiple coordination geometries, which is also evident in these structures.[43] In addition to argentophilic interactions, structures were commonly observed with solvates, especially when acetonitrile was used as the crystallization solvent. In the structure of **[6—Ag—6]SbF$_6$** (Figure S44) and **[7—Ag—7]PF$_6$** (Figure 3), the acetonitrile is bonded to the silver making it three or even four-coordinate (in case of $Ag^+\cdots Ag^+$ interactions as well). Both the argentophilic interactions and the coordinating solvates affect the $[N—Ag—N]^+$ bond angle varying it from 149.11(8)° to a symmetry enforced, perfect linear geometry of 180°.

The silver(I) complexes favour two types of packing; either a dimeric packing with argentophilic interactions or an alternating anion-ligand packing with slipped *π—π* interactions between the ligands. The positively charged silver(I) complex results, in both cases, in the anions closely interacting with the C-H of the five-membered ring (**1** – **4**) and the aromatic C-H motifs. These two types of packing are depicted in Figure 4. The interactions in the complex naturally vary depending on the ligand, anion, and solvent.

From the seven ligands investigated, iodine(I) complexes for four ligands were obtained in solid-state and all the $[N—I—N]^+$ bond lengths and angles are listed in Table S2 as well as in Figure 5. In contrast to the silver(I) complexes with varying coordination angles, the iodine(I) structures have a strong preference toward linearity due to the highly directional nature of the I^+ cation, with the largest deviation being observed for **[1—I—1]PF$_6$** with 176.9(2)°, which is still less than the previously reported $[N—I—N]^+$ bond angle of 175°.[3,32] All N—I bond lengths

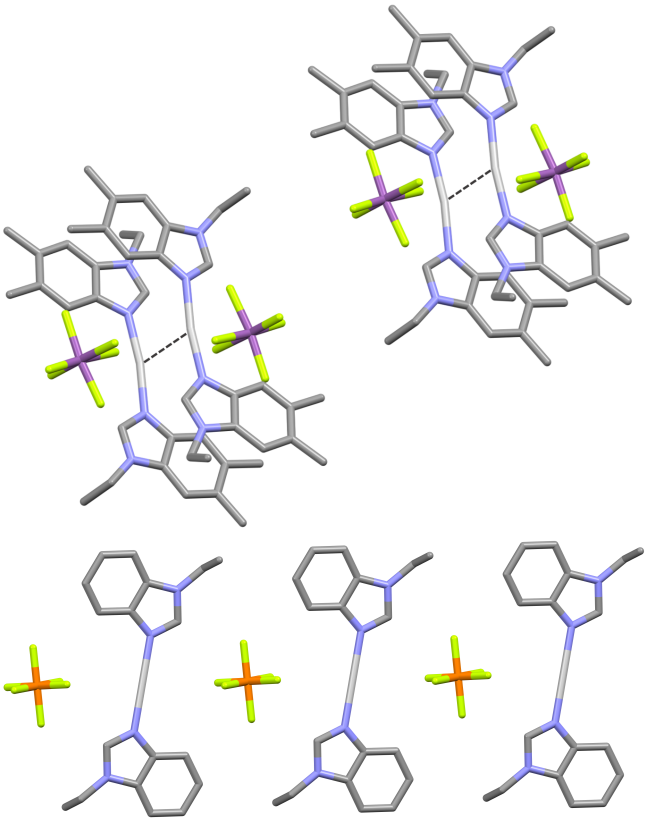

Figure 4. The packing of **[4—Ag—4] SbF$_6$** as argentophilic dimers (top) and **[2—Ag—2]PF$_6$** (bottom) as three monomers.

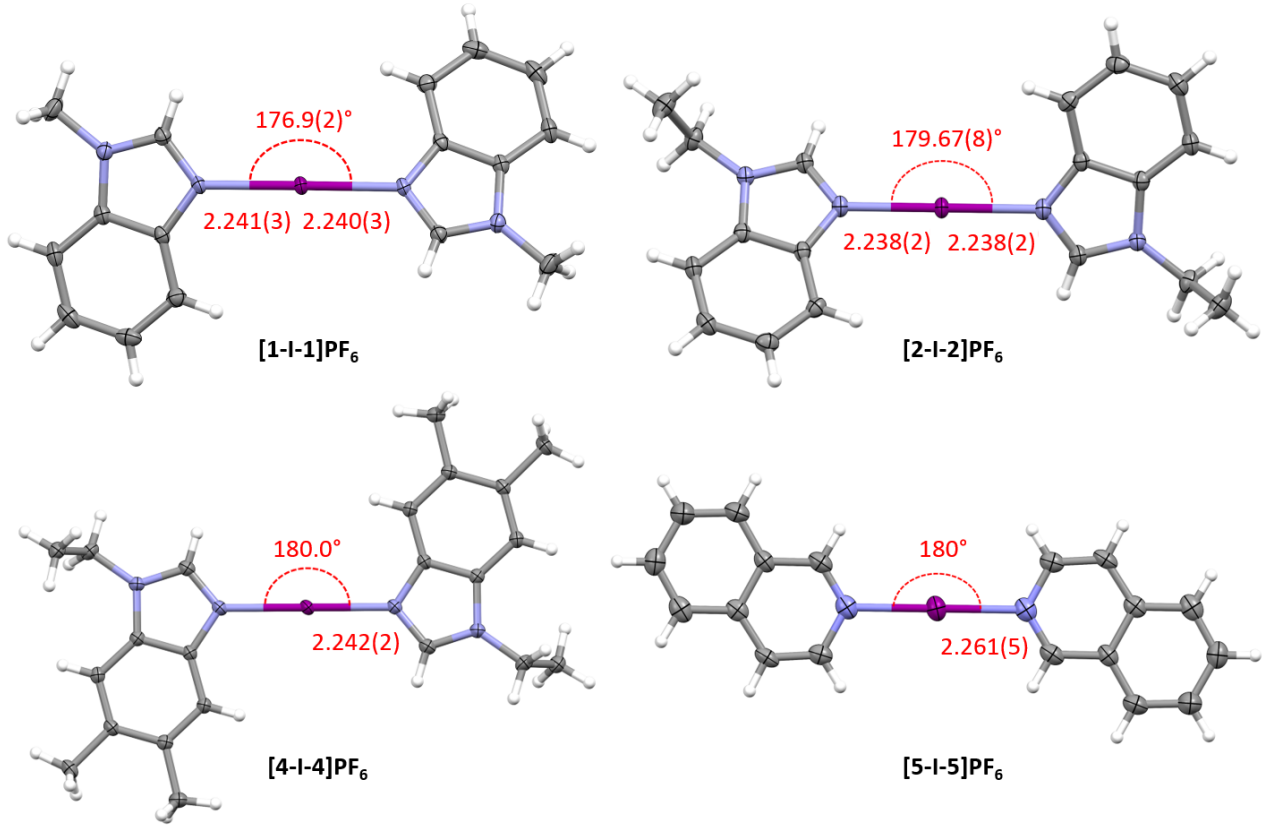

Figure 5. Single crystal X-ray structures of the determined halogen(I) complexes **[1—I—1]PF$_6$**, **[2—I—2]PF$_6$**, **[4—I—4]PF$_6$**, and **[5—I—5]PF$_6$** (counter-anions omitted for clarity. Thermal displacement ellipsoids drawn at the 50% probability level; all lengths in Å).

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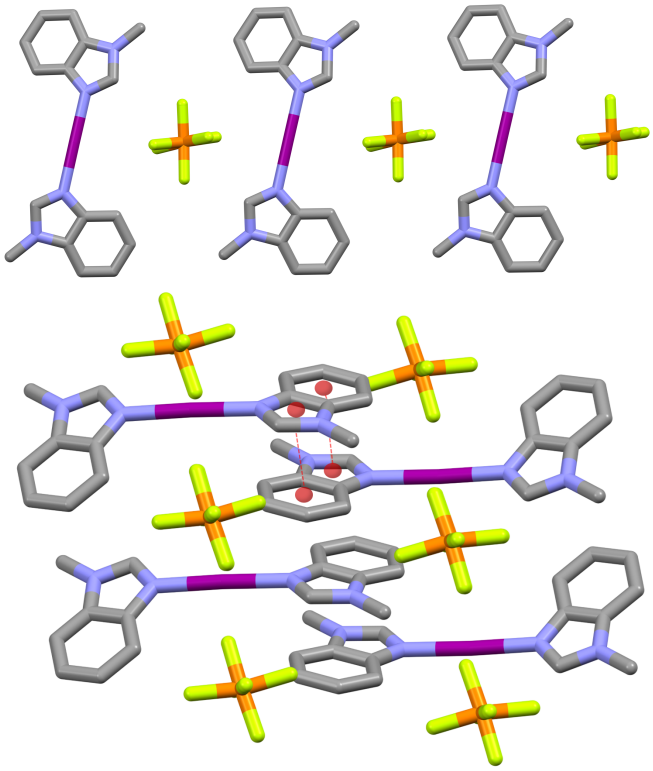

Figure 6. The packing of **[1—I—1]PF$_6$** in solid-state. Intermolecular *π–π* (centroid-centroid) interactions highlighted in red.

were also found to be within the narrow range of 2.213(3) - 2.263(3) Å, corresponding to the R_{XB} values of 0.63 - 0.64 shown in Table S3 ($R_{XB} = d_{XB}/(X_{vdW} + B_{vdW})$, where d_{XB} is the distance between the halogen atom and the electron donor, X_{vdW} is the van der Waals radii of the halogen atom and B_{vdW} is the van der Waals radii of the electron donor atom[44]). These values indicate even stronger interactions than usually reported for 3c-4e halogen(I) complexes (R_{XB} = 0.65 - 0.69, *d*(N—I) = 2.23 - 2.31 Å).[12,31]

In contrast to the silver(I) complexes, the packing of the iodine(I) complexes always occurs in the same way (Figure 6) resembling the monomeric packing pattern of the silver(I) structures with slipped *π—π* interactions between the ligands. Whereas silver(I) complexes prefer anion-coordination and argentophilic interactions, the halogen(I) complexes do not possess the required empty orbitals for such an interaction.[15] The anions in the iodine(I) complexes do not interact with the halogen(I) ions, and only affect the solubility of the species and the packing in the crystal structure.[30] Even when packing asymmetrically in solid-state, anions do not induce any effect on the symmetry of the [N—I—N]$^+$ bond.[15] Short I$^+$···I$^+$ inter-complex distances in solid-state, reminiscent to the Ag$^+$···Ag$^+$ argentophilic interactions, are very rare.[31,33] In the case of the iodine(I) complexes studied here, no short I$^+$···I$^+$ inter-complex distances were observed.

Due to the inherent reactivity of the iodine(I) ion, protonated side products are fairly common in the pursuit of iodine(I) complexes, and in this case, one protonated species **[3—H]I** of ligand **3** with iodide as a counter-anion was obtained (Figure S25). In addition, repeated attempts were made to crystallize **[6—I—6]$^+$** and **[7—I—7]$^+$**, though with no success. The larger size of the ligand and low solubility of the Ag$^+$ and I$^+$ complexes play a critical role in the crystallization of these species. Due to the weak C—H and *π—π* interactions observed for ligand **7**, crystals recovered from the crystallization of **[7—I—7]PF$_6$** were revealed to be the parent ligand itself (Figure S43). Additionally, in most cases with ligands **6** and **7**, acetonitrile was also found coordinating to the silver(I), making the N—Ag—N angles deviate from linearity (152.19(9)°).

An unusual case also arose whilst pursuing the solid-state structures, with the observation of an asymmetric **[7—Ag—MeCN]PF$_6$** complex (Figure 7), where acetonitrile coordination to the Ag$^+$ is retained despite the 2:1 stoichiometry. This rare asymmetric 2-coordinate silver(I) structure also suggests an enhanced nucleophilicity of the ligand **7**, or the existence of steric hindrance between the ligands in the close argentophilic dimer of the symmetric **[7—Ag—7]$^+$** (Figure 3) complex, making the asymmetric structure **[7—Ag—MeCN]PF$_6$** isolable as a minor product.

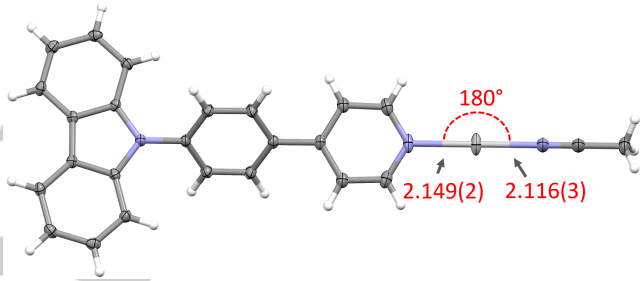

Figure 7. The asymmetric silver(I) structure of **[7—Ag—MeCN]PF$_6$** (counter-anion omitted for clarity. Thermal displacement ellipsoids drawn at the 50% probability level; all lengths in Å).

The asymmetric **[7—Ag—MeCN]PF$_6$** shows a slightly shorter bond length between the silver(I) and **7** compared to its symmetric counterpart (*cf.* 2.167(5) Å). The crystallization conditions could also affect whether asymmetric or symmetric complexes are formed. The symmetric complex was obtained from acetonitrile evaporation, whereas the asymmetric complex was obtained from an acetonitrile/dichloromethane mixture diffused with pentane at 277 K. The only similar linear two-coordinate N—Ag—CH$_3$CN complex was reported by Vögtle *et al.* more than 20 years ago.[45]

Due to the difficulties in obtaining the iodine(I) complex from ligand **6**, an alternative approach was attempted to synthesize it. It has been previously reported that the addition of elemental iodine in excess, could lead to an I$_2$ adduct formation, which eventually undergoes heterolytic cleavage of the I$_2$ to form an iodine(I) complex with a I$_3^-$ counter-anion (due to a second molecule of I$_2$).[34] This was also supported by the X-ray structure of **[5—I—5]I$_3$** (Figures S37-38). Due to the consistency with other complexes' names, the I$^+$ complex of ligand **5** is named as **[5—I—5]I$_3$** (despite there being three elemental iodine solvates in the crystal lattice, viz. **[5—I—5]**I$_3$• 3 I$_2$). For the **[5—I—5]I$_3$** complex, though the normal synthesis route was used, the resulting iodine(I) complex crystallized more readily with I$_3^-$ as the counter-anion, rather than with PF$_6^-$. However, whilst attempting to crystallize **[6—I—6]I$_3$** in the presence of excess I$_2$, a neutral halogen-bonded complex **6·I$_2$** was observed, where the I$_2$ is directly bonded to the ligand's nitrogen atom (Figure 8). For this

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complex, the N—I bond length was found to be similar (2.397(9) [46]

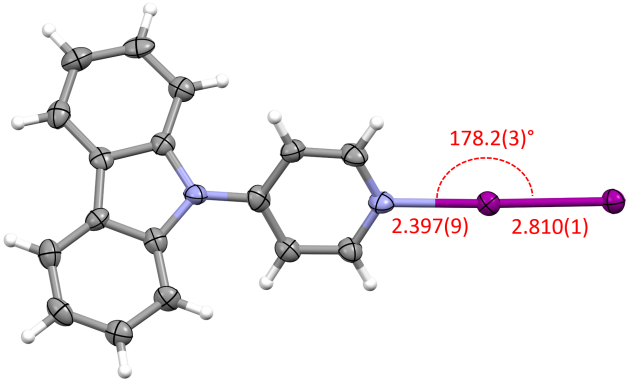

Figure 8. X-ray structure of the halogen-bonded complex **6·I₂** (thermal displacement ellipsoids drawn at the 50% probability level; all lengths in Å).

Å, R_{XB} = 0.68, Table S3) to other aromatic amine-I_2 complexes.[46] Similarly the iodine I—I bond length was found to be 2.810(1) Å, which is much longer than that of free iodine (2.715 Å) in solid-state, and in-line to those previously reported for the analogous pyridine·I_2 halogen-bonded complexes.[46]

In addition to structural studies the halogen-bonded complex **6·I₂** was further studied with UV-Vis and fluorescence spectroscopy due to the fascinating photophysical properties ligand **6** has previously revealed upon protonation.[47] In the protonation experiments of **6**,[47] the protonation was found to decrease the energy of the placement of the pyridyl unit out of the plane making the molecular rotation more accessible, as well as change the lowest lying electronic transition, which resulted in quenching of the fluorescence. However, similar behavior with the halogen-bonded species was not observed. In contrast to the protonated species, an 8% increase in the integrated fluorescence intensity was observed (Figure S47), which is most likely a result of halogen-bond assisted intramolecular charge-transfer.[48]

Conclusion

Herein, we have prepared symmetric 2-coordinate silver(I) complexes for ligands **1** – **7**, along with an asymmetric **[7—Ag—MeCN]PF₆** acetonitrile-adduct complex. Some of the ligands manifested short argentophilic interactions and were observed as dimeric complexes in the solid-state. The silver(I) complexes served as precursors to the target iodine(I) complexes. The formation of the complexes was confirmed *via* ^{1}H and ^{1}H-^{15}N HMBC NMR analyses, which showed 0.36 - 1.06 ppm changes in the ^{1}H NMR chemical shifts, and 94 - 111 ppm changes in the ^{15}N NMR chemical shifts from the ^{1}H-^{15}N HMBC measurements, upon conversion from the free ligand to an iodine(I) complex. The conversion from the ligand to the silver(I) and iodine(I) complexes lowers the solubility of the species, even in the most polar solvents such as DMSO. The crystallization process, being highly dependent on the crystallization conditions such as solvent and solubility, was unsuccessful for the few low-solubility complexes, and therefore the identity of some of the iodine(I) complexes was only confirmed in solution. However, further confirmation of the identity of the iodine(I) complexes was provided by single crystal X-ray structures for four of the ligands. The iodine(I) complexes experienced extremely strong halogen bonds with R_{XB} values of 0.63 - 0.64, even surpassing most of the previously reported 3c-4e bonded [N—I—N]$^+$ complexes. The work herein has extensively studied iodine(I) complexes of benzoimidazole and pyridylcarbazole derivatives, and despite limited solubility, demonstrated each of the ligands being capable of this interaction. The results reported here, within this fast-growing field of research, provide valuable information for the development of XB-based materials for future applications.

Experimental Section

All reagents and solvents obtained from commercial suppliers were used without further purification. Synthesis of all prepared compounds is described in the Supporting Information. For NMR assignments, ^{1}H and ^{1}H -^{15}N HMBC NMR spectra were recorded using either Bruker 300 Avance or Bruker Avance III 500 MHz spectrometer at 303 K. Chemical shifts are reported on the δ scale in ppm using the residual solvent signal as internal standard ($CDCl_3$, δH 7.26; CD_2Cl_2, δH 5.32; CD_3CN, δH 1.94; $(CD_3)_2CO$, δH 2.05; DMSO-d_6, δH 2.50). For ^{15}N NMR, CD_3NO_2 is used as an external reference. For ^{1}H NMR spectroscopy, each resonance was assigned according to the following conventions: chemical shift (δ) measured in ppm, observed multiplicity, number of hydrogens, observed coupling constant (J Hz), and assignment. Multiplicities are denoted as s (singlet), d (doublet), t (triplet), q (quartet) m (multiplet), and br (broad).

The UV-Vis and fluorescence studies of **6·I₂** were performed at room temperature. Absorption spectra were collected using a Varian Cary 100, 300 Series II Series UV-Visible Spectrophotometer, and fluorescence spectra were collected using a Varian Cary Eclipse Fluorescence Spectrophotometer. The measurements were taken in a 1 cm quartz cuvette and the excitation and the emission bandpasses were set to 2.5 nm and 2.5 nm, respectively.

The single crystal X-ray crystallographic experimental and refinement details for all complexes are given in the Supporting Information. Deposition Number(s) 2106003 (for **[1—Ag—1]PF₆**), 2106004 (for **[1—I—1]PF₆**), 2106005 (for **[1—I—1]PF₆_2**), 2106006 (for **[2—Ag—2]PF₆**), 2106007 (for **[2—Ag—2]PF₆_2**), 2106008 (for **[2—I—2]PF₆**), 2106009 (for **3**), 2106010 (for **[3—Ag—3]PF₆**), 2106011 (for **[3—H]I**), 2106012 (for **4**), 2106013 (for **[4—Ag—4]SbF₆**), 2106014 (for **[4—I—4]PF₆**), 2106015 (for **[5—Ag—5]PF₆**), 2106358 (for **[5—Ag—5]BF₄**), 2106359 (for **[5—Ag—5]OTf**), 2106360 (for **[5—I—5]PF₆**), 2106361 (for **[5—I—5]BF₄**), 2106362 (for **[5—I—5]OTf**), 2106016 (for **[5—I—5]I₃**), 2080281 (for **6**), 2106017 (for **[6—Ag—6]PF₆**), 2106018 (for **[6—Ag—6]BF₄**), 2106019 for (**[6—Ag—6]SbF₆**), 2106020 (for **6·I₂**), 2080282 (for **7**), 2106021 (for **[7—Ag—7]PF₆**), and 2106022 (for **[7—Ag—MeCN]PF₆**) contain the supplementary crystallographic data. These data can be obtained free of charge by The Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe.

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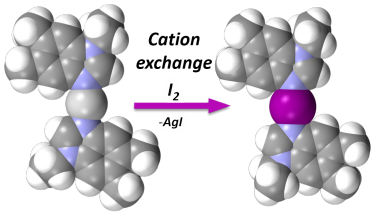

Silver(I) complexes of benzoimidazole and carbazole-derived *sp*^{2} *N*-containing Lewis bases are synthesized and the isostructural iodine(I) complexes with a strong 3-center 4-electron $[N–I–N]^+$ halogen bond are obtained through the $[N–Ag–N]^+ \rightarrow [N–I–N]^+$ cation exchange reaction. The unambiguous confirmation of the complex formation is obtained in the solution state using NMR spectroscopy, and in the solid-state, with single crystal X-ray diffraction.

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