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Introduction

The halogen-bonding (XB) interaction, a type of non-covalent interaction, only started to draw attention in the 1990s due to the work by the groups of Metrangolo and Resnati,^{1,2} and Legon^{3,4} among others.^{5,6} Nowadays, because of the unique features of halogen bonding, such as directionality, a tuneable interaction strength, and an understanding of the utility of XB, it is becoming a booming topic in many fields, for instance supramolecular chemistry,^{7–9} medicinal chemistry,^{10–13} materials sciences,^{14–17} and organic synthesis and catalysis.^{18–22}

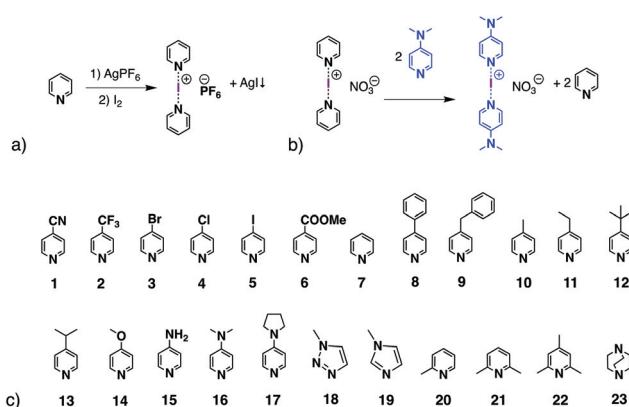
The halogen(i) complex, formed with a halenium ion (X^+ , where $X = \text{Cl, Br, I}$) and two Lewis bases in a linear fashion $[L\cdots X\cdots L]^+$, is considered as one of the strongest halogen-bond complexes, along with those XB complexes using perfluorocarbons (PFHCs)^{1,2,23} or *N*-halosaccharin^{24,25} as XB donors. Barluenga's eponymous reagent, $[\text{I}(\text{Py})_2][\text{BF}_4]$ (Py = pyridine),²⁶ which can be viewed as the archetypal halogen(i) complex, is known in synthetic chemistry as an iodinating and oxidising agent.^{27–30} Among the five halogens, iodine(i), bromine(i), and chlorine(i) have been reported to form three-centre-four-electron (3c-4e) bonds as $[L\cdots X\cdots L]^+$ complexes, whereas fluorine(i) has been studied and was found to prefer conventional

Ligand exchange among iodine(i) complexes†

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A detailed investigation of ligand exchange between iodine(i) ions in $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ halogen-bonded complexes is presented. Ligand exchange reactions were conducted to successfully confirm whether iodine(i) complex formation, via the classical $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange reaction from their analogous Ag^+ complexes, could be determined solely by using ^1H NMR spectroscopy. In instances where the formation of the iodine(i) complex was unclear or in low yield by the traditional cation exchange reaction, a ligand exchange reaction was used to form the desired iodine(i) complexes in a quantitative manner. Mixing two homoleptic $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ iodine(i) complexes in 1:1 ratio was found to undergo a statistical ligand exchange, with ^1H NMR studies showing that the preferred formation of the relative heteroleptic $[\text{N}_1\cdots\text{I}\cdots\text{N}_2]^+$ complexes increases with greater differences in the Lewis basicities of two XB acceptors of the complexes involved.

halogen bonds of the form $\text{L}^+\cdots\text{F}\cdots\text{L}$,³¹ and astatine has been found to behave as a stronger halogen-bond donor than iodine both experimentally and computationally.³² The iodine(i) and bromine(i) complexes, predominantly of the $[\text{N}\cdots\text{X}\cdots\text{N}]^+$ motif ($\text{X} = \text{Br, I}$),³³ are stable at ambient conditions and can be prepared by the classical $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange reaction from their analogous Ag^+ complexes (Scheme 1a). The geometries of homoleptic $[\text{N}\cdots\text{X}\cdots\text{N}]^+$ complexes ($\text{X} = \text{Cl, Br, I}$) have been extensively studied by Erdélyi and coworkers.^{31,34–36} Considering the halogen(i) complexes possible from the myriad of potential ligands, the reported halogen(i) complexes in the CSD database are still limited.^{37–42} The difficulty in obtaining single crystals of halogen(i)



Scheme 1 (a) Synthesis of iodine(i)-nitrogen, $[\text{N}\cdots\text{I}\cdots\text{N}]^+$, complexes, using pyridine as a general example; (b) ligand exchange reaction of pyridine for DMAP about an $[\text{I}]^+$, reported by Dutton *et al.*; (c) list of ligands 1–23 used in this work.

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complexes sometimes makes it challenging to prove their formation, unless more definitive methods were available in solution. It has been reported that the ^{15}N NMR chemical shift change of the coordinated nitrogen can indicate the formation of an $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ complex,⁴³ though not always conclusively, as the ^{15}N NMR chemical shift changes of the nitrogen atom in some protonated ligands also fall within similar expected ranges.⁴⁴ Whilst the $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange reaction is reliable for many substituted pyridines,⁴² it is not effective for all ligand types. With this classic method of preparation, the $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ complexes of some ligands can be afforded in low yield, but in conjunction with the protonated ligands as side products. These side products further complicate attempts to identify them solely based on the ^1H NMR data, especially when the formed protonated ligands are often more amenable to recrystallisation, which can be a false indicator that the reactions have failed to produce the desired $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ complexes.

In 2013 Dutton and co-workers reported the formation of the $[\text{I}(\text{DMAP})_2][\text{NO}_3]$ iodine(i) complex (DMAP = 4-dimethylaminopyridine; Scheme 1b) in a 71% yield, achieved by adding the free DMAP ligand into a solution of $[\text{I}(\text{Py})_2][\text{NO}_3]$.⁴⁵ Furthermore, the UV-Vis kinetics of the dissociation of several pyridine-iodine(i) complexes in the presence of DMAP have been studied by Erdélyi and co-workers.³⁶ Using the strategy of molecular clefts, heteroleptic halogen(i) complexes have been prepared,⁴⁶ however, only very recently was the first unrestrained heteroleptic iodine(i) complex confirmed in the solid state,³⁸ and following that was further studied in solution by the Erdélyi group.⁴⁷ They concluded that the preference of iodine(i) was to form complexes with the more basic pyridine, which proceeded at slower ligand exchange rates; the mixing of two homoleptic halogen-bonded iodine(i) complexes leads to a statistical distribution of the pyridine ligands across the iodine(i) ions. Recently the utility of ligand exchange of discrete iodine(i) complexes has been demonstrated as an effective means to synthesise rare examples of iodine(i) macrocycles.⁴⁸

Herein we present a comprehensive investigation of the ligand exchange reactions in iodine(i) complexes, the identity of which can be confirmed solely by ^1H NMR spectroscopy using a strong Lewis base (e.g., DMAP). The exchange was determined to be quantitative in the conversion, despite iodine(i) complexes being used as the electrophilic reagent. The efficacy of the ligand exchange process was found to be strongly dependent on the difference of Lewis basicities between the two ligands involved. In some cases, the ligand exchange yields a more informative synthetic methodology when compared with the traditional $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange reaction, as the ligand exchange process is more readily monitored. In addition, it was found that when the difference of the XB acceptor basicities in the iodine(i) system increases, a higher percentage of the heteroleptic iodine(i) complexes were formed, with greater covalent bond character between the iodine(i) and the XB acceptor possessing the higher Lewis basicity.

Results and discussion

Ligand exchange of iodine(i) complexes

These studies tested 23 ligands (Scheme 1c) to thoroughly investigate the ligand exchange behaviour of iodine(i) complexes. The free ligand DMAP (**16**) and iodine(i) complex $[\text{I}(\text{7})_2]\text{PF}_6$ were chosen to represent the ligand exchange behaviour in the solution state, as the ^1H NMR chemical shifts of complexes $[\text{I}(\text{16})_2]\text{PF}_6$, $[\text{I}(\text{7})_2]\text{PF}_6$ and $[\text{I}(\text{7})(\text{16})]\text{PF}_6$ are known,³⁸ and the formation of $[\text{I}(\text{16})_2]\text{NO}_3$ through a ligand exchange reaction of $[\text{I}(\text{7})_2]\text{NO}_3$ and **16** was already performed by Dutton and co-workers.⁴⁵ The symmetrical iodine(i) complex $[\text{I}(\text{7})_2]\text{PF}_6$ itself was prepared *via* the traditional $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange reaction (Fig. 1a). As shown in Fig. 1b–e, with the addition of the free ligand DMAP (**16**; 0.5, 1.0, 1.5, and 2.0 equivalents) into the solution of $[\text{I}(\text{7})_2]^+$, the ^1H NMR spectra showed the gradual decrease of the peaks of $[\text{I}(\text{7})_2]^+$ until it completely disappeared. Concomitantly a new set of signals for **7** appeared (Fig. 1b), increased (Fig. 1c), decreased (Fig. 1d), and finally disappeared (Fig. 1e), with the chemical shifts in agreement with the previously reported values for asymmetrical complex $[\text{I}(\text{7})(\text{16})]^+$ (green trace).³⁸ The green peaks of **16** in $[\text{I}(\text{7})(\text{16})]^+$, which follows the same trend as the green **7**, also supports that assignment. The signals for $[\text{I}(\text{16})_2]^+$ (blue trace) appeared later than the $[\text{I}(\text{7})(\text{16})]^+$ signals, and kept increasing until the complete consumption of the $[\text{I}(\text{7})(\text{16})]^+$ species (green trace). The signals of **7** (black trace) increased and moved towards the chemical shifts observed for **7** as a free ligand, due to the increase of **7** being released in the reaction caused by the ligand exchange (for more detailed information, see Fig. S18†). When the ligand exchange reaches completion, the exchange yield of iodine(i) cation is 100%. From the above analysis, it is clear that before the full ligand

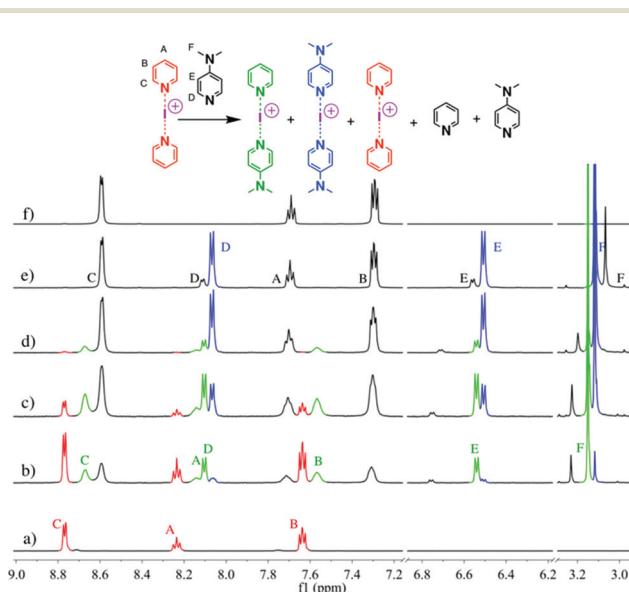


Fig. 1 ^1H NMR spectra (500 MHz, CD_2Cl_2 , $30\text{ }^\circ\text{C}$) of pure $[\text{I}(\text{7})_2]\text{PF}_6$ (a) and $[\text{I}(\text{7})_2]\text{PF}_6$ in the presence of 0.5 (b), 1.0 (c), 1.5 (d), and 2.0 equivalents (e) of **16**, and of pure **7** (f).



exchange, the heteroleptic iodine(i) complex was first formed as the intermediate.^{38,47,49}

The signals of **7** in $[\text{I}(7)(\mathbf{16})]^+$ (green trace) has shifted towards upfield when compared to $[\text{I}(7)_2]^+$; whilst the signals of **16** in $[\text{I}(7)(\mathbf{16})]^+$ (green trace) has shifted downfield when compared to $[\text{I}(16)_2]^+$. This can be explained as the asymmetry of the N–I–N bond in $[\text{I}(7)(\mathbf{16})]^+$ that causes a different extent of electron donation from **7** in $[\text{I}(7)_2]^+$ and **16** in $[\text{I}(16)_2]^+$ as compared to $[\text{I}(7)(\mathbf{16})]^+$. As the iodine(i) cation gets more electrons from **16**, it will pull less from **7**.

Ligands **1–6**, **8–14** and **18–23** were also used to prepare the relevant iodine(i) complexes *via* the $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange reaction (see Section 2 in ESI†). The formation of $[\text{I}(\mathbf{L})_2]^+$ ($\mathbf{L} = \mathbf{8–14}$, **18–19**) are clean and were further confirmed through ligand exchange reactions. The reactions of $[\text{I}(\mathbf{L})_2]^+$ ($\mathbf{L} = \mathbf{1–6}$, **20**) were not particularly clean, but the ligand exchange process can monitor what components are present and which parts belong to the desired iodine(i) complexes. $[\text{I}(10)_2]\text{PF}_6$ was used to form iodine(i) complexes $[\text{I}(15)_2]^+$ and $[\text{I}(17)_2]^+$ *via* ligand exchange reactions.

As shown in Fig. S45, S50† and Fig. 2a, the reactions of $[\text{I}(\mathbf{L})_2]^+$ ($\mathbf{L} = \mathbf{21, 22, 23}$) from the traditional $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange method did not proceed cleanly, while *via* the ligand exchange reaction between ligand **21** or **22** and the complex $[\text{I}(18)_2]^+$, which had a less basic ligand than **21** and **22**, clean complexes of $[\text{I}(21)_2]^+$ and $[\text{I}(22)_2]^+$ were readily afforded (Fig. S46, S48, S51 and S53†). Additionally, using the same method, the complex of **23**, $[\text{I}(23)_2]^+$, was also obtained (Fig. 2b, S55 and S56†), and further confirmed by the single crystal X-ray structure analysis (Fig. S67†).

The efficacy of the iodine(i) ion transfer strongly depends on the Lewis basicities of the two involved ligands, as well as the stoichiometries of the iodine(i) complex and the free ligand. For example, with 20 eq. of **10** being introduced to 1 eq. of $[\text{I}(16)_2]\text{PF}_6$, no trace of $[\text{I}(10)_2]\text{PF}_6$ was observed.

However, the addition of 2 eq. of free ligand **16** into 1 eq. of $[\text{I}(10)_2]\text{PF}_6$ causes the full iodine(i) ion transfer, whilst 3 eq. of the free ligand **16** were required with 1 eq. of $[\text{I}(14)_2]\text{PF}_6$ to exclusively yield $[\text{I}(16)_2]\text{PF}_6$.

It is noteworthy that, despite its reactive nature, the iodine(i) ion transfer was quantitative among all cases studied in this work, indicating the strong coordinative character of the iodine(i) ion. Among all of the above cases, the chemical shift of **16** in the homoleptic and multiple heteroleptic complexes, in each individual case, does not change during the whole process of ligand exchange when the ratios of the different species are changing. This is due to the slow exchange rate of ligand **16** in the iodine(i) complexes, as well as other experimental factors.⁴⁷

Homoleptic versus heteroleptic preference in iodine(i) complexes

In a previous study,⁴⁷ two homoleptic iodine(i) complexes, $[\text{I}(2)_2]^+$ and $[\text{I}(7)_2]^+$, were mixed together in different ratios to evaluate the resulting ratios of $[\text{I}(2)_2]^+$, $[\text{I}(7)_2]^+$, and freshly generated $[\text{I}(2)(7)]^+$, by integration of the corresponding ^1H NMR signals. From this they concluded that the ligand exchange proceeds due to a dominant entropic contribution. Herein, the difference of basicities of the two XB acceptors involved were investigated to see if they have an influence on the distribution of the homoleptic and heteroleptic species observed. The molar ratios of $[\text{I}(\mathbf{L})_2]^+$, $[\text{I}(16)_2]^+$, and $[\text{I}(\mathbf{L})(\mathbf{16})]^+$ in solution were analysed by mixing complexes of $[\text{I}(16)_2]^+$ and $[\text{I}(\mathbf{L})_2]^+$ ($\mathbf{L} = \mathbf{1, 7, 12, 15, 18}$) in a 1 : 1 ratio (Table 1). Surprisingly, as the Lewis basicities of ligand **L** decreases in the order of **15** (4-NH₂Py) > **12** (4-*t*BuPy) > **7** (Py) > **18** (triazole) > **1** (4-CNPy), the percentage of the heteroleptic species $[\text{I}(\mathbf{L})(\mathbf{16})]^+$ among the iodine(i) complexes was found to increase. Meanwhile, the signals of the free ligands **L** and **16** start to appear and increase for $\mathbf{L} = \mathbf{7, 18, 1}$, suggesting that the heteroleptic complexes $[\text{I}(\mathbf{L})(\mathbf{16})]^+$ were getting less stable upon increasing the difference of basicities of the two Lewis bases involved. The slightly pink colours of those reactions also support that, as elemental iodine is generated by the reaction.

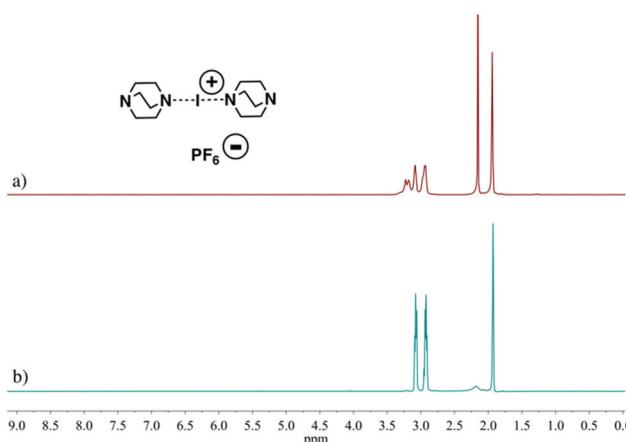


Fig. 2 The ^1H NMR spectra (500 MHz, CD_3CN , 30 °C) of the crude mixture of reaction $[\text{I}(23)_2]\text{PF}_6$ by the traditional $[\text{N}\cdots\text{Ag}\cdots\text{N}]^+$ to $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ cation exchange reaction (a) and the pure iodine(i) complex $[\text{I}(23)_2]\text{PF}_6$ prepared from the ligand exchange reaction between $[\text{I}(18)_2]\text{PF}_6$ and free ligand **23** (b).

Table 1 The molar ratios of $[\text{I}(\mathbf{L})_2]^+$, $[\text{I}(16)_2]^+$ and $[\text{I}(\mathbf{L})(\mathbf{16})]^+$ in solution after mixing 1 : 1 complexes $[\text{I}(16)_2]^+$ and $[\text{I}(\mathbf{L})_2]^+$ ($\mathbf{L} = \mathbf{1, 7, 12, 15, 18}$); the comparisons of the ^{15}N chemical shift values of pyridinic nitrogen in **16** for the homoleptic complex $[\text{I}(16)_2]^+$, and the heteroleptic complexes $[\text{I}(\mathbf{L})(\mathbf{16})]^+$ ($\mathbf{L} = \mathbf{1, 7, 12, 15, 18}$)

Comp.	$[\text{I}(\mathbf{L})_2]^+ : [\text{I}(\mathbf{L})(\mathbf{16})]^+ : [\text{I}(16)_2]^+$	$\Delta\delta^a$	$\Delta\Delta\delta^b$
$[\text{I}(16)_2]^+$	—	-107.6 (-110.7) ^c	0
$[\text{I}(15)(\mathbf{16})]^+$	1 : 2.2 : 1 (52.4%) ^c	-112.7 ^c	-2.0 ^c
$[\text{I}(12)(\mathbf{16})]^+$	1 : 3.2 : 1 (61.5%)	-123.6	-16.3
$[\text{I}(7)(\mathbf{16})]^+$	1 : 4.8 : 1 (70.6%)	-128.3	-21.0
$[\text{I}(18)(\mathbf{16})]^+$	1 : 9.5 : 1 (82.6%)	-135.0	-27.4
$[\text{I}(1)(\mathbf{16})]^+$	1 : 23.5 : 1.2 (91.4%) ^d	-143.4	-35.8

^a The ^{15}N NMR chemical shift change of pyridinic nitrogen of DMAP upon complexation. ^b $\Delta\Delta\delta = \Delta\delta([\text{I}(\mathbf{L})(\mathbf{16})]^+) - \Delta\delta([\text{I}(16)_2]^+)$. ^c Performed in CD_3CN . ^d Protonated or free ligands excluded.



The ^{15}N NMR chemical shift values based on the ^1H - ^{15}N HMBC measurements of the pyridinic nitrogen of DMAP (**16**) in the heteroleptic complexes $[\text{I}(\text{L})(\text{16})]^+$ ($\text{L} = 1, 7, 12, 15, 18$) are also summarised in Table 1. The complexation-induced chemical shift change, $\Delta\delta_{\text{N}}$, defined as $\delta^{(15)\text{N}_{\text{complex}}}) - \delta^{(15)\text{N}_{\text{DMAP}}})$, gets larger when decreasing the Lewis basicity of ligand L in the same order as previously described ($15 > 12 > 7 > 18 > 1$; *vide supra*), indicating the increasing electron density around the pyridinic nitrogen of DMAP (**16**). Even larger $\Delta\delta_{\text{N}}$ values, up to -135.0 ppm were observed for $[\text{I}(\text{18})(\text{16})]^+$ (*cf.* $[\text{I}(\text{1})(\text{16})]^+ = -143.4$ ppm), than those previously reported for the stabilised O–I–N complex $\text{F}_3\text{CC}(\text{O})(\text{O}i\text{-DMAP})$, which had a value of -129 ppm.⁴⁴ The $\Delta\delta$ values of the pyridinic nitrogen atoms of the weaker Lewis bases of the heteroleptic complexes $[\text{I}(\text{15})(\text{16})]^+$, $[\text{I}(\text{12})(\text{16})]^+$ and $[\text{I}(\text{7})(\text{16})]^+$ were also recorded (Table S1†). The deshielding of the ^{15}N NMR signals of weaker Lewis bases in $[\text{I}(\text{15})(\text{16})]^+$, $[\text{I}(\text{12})(\text{16})]^+$, and $[\text{I}(\text{7})(\text{16})]^+$ as compared to the respective homoleptic complexes, $[\text{I}(\text{15})_2]^+$, $[\text{I}(\text{12})_2]^+$ and $[\text{I}(\text{7})_2]^+$, were as expected. The values for $[\text{I}(\text{18})(\text{16})]^+$ and $[\text{I}(\text{1})(\text{16})]^+$ were unable to be determined due to the signal coalescence (Fig. S64 and S66†).

The single crystal of $[\text{I}(\text{18})(\text{16})]\text{PF}_6$ was successfully obtained from dichloromethane upon slow evaporation (Fig. 3), only the second solid-state example of an unrestrained heteroleptic $[\text{N}_1\cdots\text{I}\cdots\text{N}_2]^+$ complex, which had two crystallographically independent molecules in the asymmetric unit cell. A comparison of the I–N bond lengths between $[\text{I}(\text{18})(\text{16})]^+$ ($2.335(8)/2.340$ Å for $\text{N}(\text{18})\text{--I}$, $2.187(8)/2.163(8)$ Å for $\text{I}\text{--N}(\text{16})$), and the symmetric analogues $[\text{I}(\text{18})_2]^+$ ($2.238(2)$ Å)⁵⁰ and $[\text{I}(\text{16})_2]^+$ ($2.236(3)/2.251(3)$

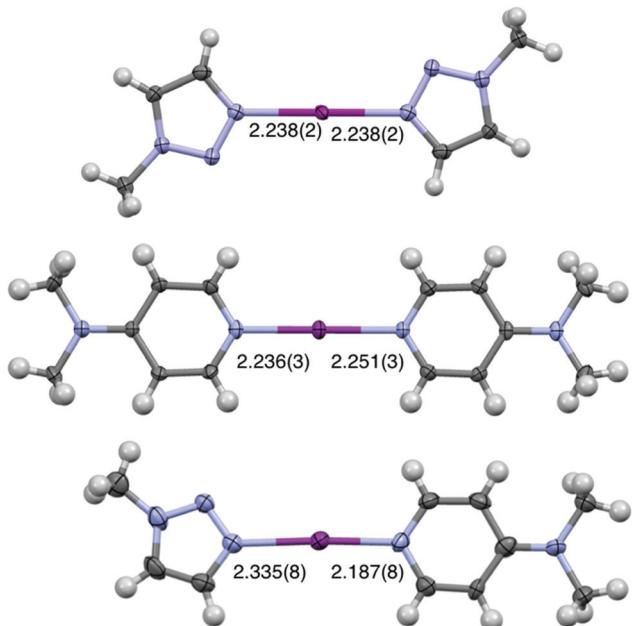


Fig. 3 The X-ray crystal structures of (from top to bottom) $[(\text{18})_2]\text{PF}_6$, $[(\text{16})_2]\text{PF}_6$, and $[(\text{18})(\text{16})]\text{PF}_6$ (PF_6 anions omitted for clarity; all lengths in Å; thermal displacement parameters at 50% probability).^{38,50} The second crystallographically independent molecule of $[(\text{18})(\text{16})]\text{PF}_6$ has been omitted for clarity ($\text{I}\text{--N}(\text{16}) = 2.163(8)$ Å, $\text{I}\text{--N}(\text{18}) = 2.340(8)$ Å).

Å),³⁸ reveal that the I–N bond length in $[\text{I}(\text{18})(\text{16})]^+$ is shortened. Consistent with the strictly linear geometry of the homoleptic 3c-4e $[\text{N}\cdots\text{I}\cdots\text{N}]^+$ halogen bonds, the angle of the N–I–N in $[\text{I}(\text{18})(\text{16})]^+$ falls within the same range with values of $178.1(4)^\circ$ and $177.0(4)^\circ$.^{37,38} However, the single crystal structure of the only other reported heteroleptic $[\text{N}_1\cdots\text{I}\cdots\text{N}_2]^+$ complex, $[\text{I}(\text{7})(\text{16})]^+$, showed the reversed I–N bond lengths changes.³⁸ Compared with I–N bond lengths in $[\text{I}(\text{7})_2]^+$ and $[\text{I}(\text{16})_2]^+$, the I–N bond length of **16** in $[\text{I}(\text{7})(\text{16})]^+$ was slightly elongated, and the I–N bond length of **7** in $[\text{I}(\text{7})(\text{16})]^+$ was slightly shortened in the asymmetric complex. This is probably due to the smaller difference of Lewis basicities between **7** and **16**, as well as the influence of the unique packing interactions.

The DFT geometries of $[\text{I}(\text{L})(\text{16})]^+$ ($\text{L} = 1, 7, 12, 15, 16, 18$) (Fig. 4) were calculated using the experimentally determined coordinates for the purpose of comparison, as had been

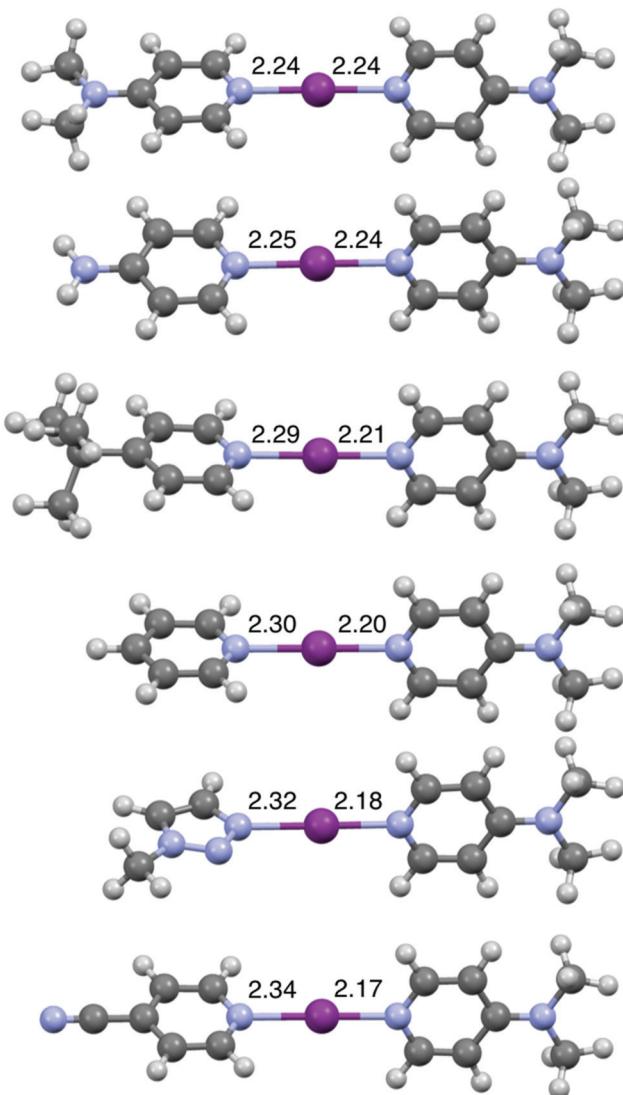
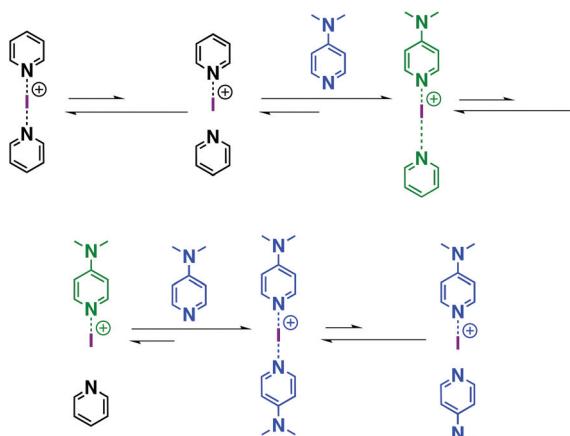


Fig. 4 The computationally generated structures for $[(\text{16})_2]^+$ and $[\text{I}(\text{L})(\text{16})]^+$ ($\text{L} = 15, 12, 7, 18, 1$) (in order of decreasing Lewis basicity from top to bottom), with the annotated N–I lengths in Å.

reported previously for O–I–N halogen-bonded complexes.^{44,51} These calculations were performed to the M06-2X (def2-TZVP) level of theory, including a non-polar (DCM) solvent model, using the Spartan20 software package.⁵² The calculated models were all in good agreement with the experimentally determined structures obtained by X-ray crystallography, including the one for $[I(18)(16)]^+$ (Fig. 3 and S70†).^{44,51} As shown in Fig. 4, upon decreasing the Lewis basicity of ligand **L** in the order of **16** (DMAP) > **15** (4-NH₂Py) > **12** (4-tBuPy) > **7** (Py) > **18** (triazole) > **1** (4-CNPy), the N(**L**)–I bond length increases and the I–N(**16**) bond length decreases. This is consistent with the solution results (¹H and ¹⁵N NMR chemical shift changes of ligand **16** in the relative complexes $[I(L)(16)]^+$; Table 1). It should be noted that despite the increasing asymmetry of the N₁–I–N₂ bond, the N₁–I–N₂ angle remains strictly linear (Table S2†) even for $[I(1)(16)]^+$, enforced by the nature of the 3c-4e $[N_1 \cdots I \cdots N_2]^+$ halogen bond in all halogen(i) complexes.^{36–40,42,50,53}

Mechanism of ligand exchange

Similar to proposed mechanisms for halogen(i) transfer using three-centre iodine(i) complexes in organic synthesis,^{54–59} the ligand exchange process in iodine(i) complexes can be addressed (Scheme 2). The reversible dissociation of the three-centre complex (e.g., $[I(7)_2]^+$) causes the formation of free ligand **7** and an *N*-iodopyridinium cation $[I-7]^+$ as the intermediate, which is subsequently captured by the strong XB acceptor (e.g., **16**), leading to the formation of a heteroleptic halogen-bonded complex, *viz.* $[I(7)(16)]^+$. Following this reasoning, $[I(7)(16)]^+$ reversibly dissociates into free ligand **7** and an *N*-iodopyridinium cation $[I-16]^+$, which interacts with another XB acceptor **16**, forming a new homoleptic iodine complex $[I(16)_2]^+$. It should be noted that the dynamic character of the bis(acyloxy)iodates(i)-related axles in rotaxanes was also studied by the group of Šindelář, in which the carbonyl hypoiodite was analogously suggested to be the key intermediate in the transfer of the iodine(i) ion among different axles.⁶⁰



Scheme 2 The proposed mechanism of the ligand exchange process.

Conclusions

In this work, the iodine(i) cation was found to be an extraordinarily strong halogen bond donor that can be transferred among different ligands in a quantitative manner. A straightforward ligand exchange approach to synthesise and distinguish the formation of iodine(i) complexes exclusively by ¹H NMR spectroscopy has been developed. This ligand exchange method can also be used to produce iodine(i) complexes that are not viable through the traditional $[N \cdots Ag \cdots N]^+$ to $[N \cdots I \cdots N]^+$ cation exchange reaction. The ligand exchange process represents a milder synthetic approach toward the synthesis of iodine(i) complexes when compared to the now ubiquitous cation exchange process. In stoichiometric mixtures of two homoleptic iodine(i) complexes, as the difference in basicities of the XB acceptors increases, the preference toward heteroleptic products increases, along with the increasing asymmetry of the $[N_1 \cdots I \cdots N_2]^+$ bond. The extensive studies of the ligand exchange process described in this work provides more information on the coordinative character of the iodine(i) ion, and will definitely aid in the construction of iodine(i)-based supramolecular structures, a field which is just beginning to gain traction, and is now picking up speed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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