

# Fluoro and Trifluoromethyl Benzoyl Hypoiodite Complexes with Substituted Pyridines

Václav Kolařík,<sup>[a, b]</sup> Kari Rissanen,<sup>[a]</sup> and Jas S. Ward<sup>\*[a]</sup>

Based on the prior observation of the trifluoroacetate hypoiodite,  $\text{CF}_3\text{C}(\text{O})\text{OI}$ , demonstrating the largest  $\sigma$ -hole of a neutral halogen bond donor, a series of *mono*- and *bis*-carbonyl hypoiodites utilising trifluoromethyl or fluorine substituents at various positions of a parent benzoyl skeleton have been synthesised. The carbonyl hypoiodite complexes were prepared via cation exchange of the silver(I) cations with iodine(I) from the respective silver(I) carboxylates and dicarboxylates as the synthetic precursors. A range of pyridinic Lewis bases of varying

nucleophilicities were used to stabilise the carbonyl hypoiodites to further probe their properties. The silver(I) intermediates with these Lewis bases were also isolated for silver(I) pentafluorobenzoate, providing additional insight into the cation exchange reaction. All complexes were characterised both in solution ( $^1\text{H}$ ,  $^1\text{H}$ - $^{15}\text{N}$  HMBC,  $^{19}\text{F}$ ) and in the solid state (SCXRD), permitting insights into the formation of the elusive pyridine-iodine(I) cation.

## Introduction

The field of halogen bonding (XB) has risen to be one of the most studied non-covalent interactions,<sup>[1,2]</sup> subordinate only to the ubiquitous hydrogen bonding. Nevertheless, halogen bonding does enjoy some advantages over its more popular sibling, such as a high degree of linear directionality in its bonding, owing to the presence of a  $\sigma$ -hole on the halogen atom of R–X bonds, which is the positive electrostatic potential of lower electron density located directly opposite to the axis of the covalent bond of the halogen atom.<sup>[3–5]</sup> These properties have directly contributed to halogen bonding being utilised in a myriad of applications including the self-assembly of supramolecular architectures,<sup>[6–9]</sup> and even the recent development of generating such species in an environmentally-friendly fashion via mechanochemical methods.<sup>[10]</sup>

Halogen bonding is defined as the interaction between the electrophilic region of a halogen atom and a neutral or anionic nucleophile.<sup>[11]</sup> The terminal example of halogen bonding is the complete ionisation of a halogen atom to a formally 1+ oxidation state,  $\text{X}^+$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), stabilised by a pair of Lewis bases (L).<sup>[12–16]</sup> These halogen(I) (or *halonium*),  $[\text{L}–\text{X}–\text{L}]^+$ , complexes can exhibit good stability, despite their use as halogen-

ation reagents, with the most iconic example being that of *Barluenga's reagent*,  $[\text{I}(\text{py})_2]\text{BF}_4$  ( $\text{py} = \text{pyridine}$ ),<sup>[17]</sup> which is a commercially available oxidation and iodination reagent used extensively to effect a variety of organic transformations.<sup>[18–20]</sup> The strength of the halogen bonds in halogen(I) complexes follows the trend of  $\text{I} > \text{Br} \gg \text{Cl}$ , with the most examples of halogen(I) complexes in the solid state being that of iodine(I),<sup>[21]</sup> with only a few recent examples of chlorine(I) complexes by Riedel and co-workers.<sup>[22]</sup> However, these chlorine(I) complexes could be characterised as Lewis base stabilised pyridine-chlorine(I) (*N*-chloropyridinium) ions due to the highly asymmetric nature in the  $\text{Cl}–\text{N}$  bond lengths of  $[\text{Cl}(\text{py})_2]\text{BF}_4$ .<sup>[21,22]</sup>

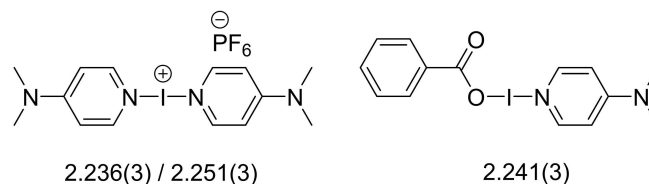
The use of *in situ* prepared hypoiodites as iodination reagents has been previously reported,<sup>[23]</sup> though often the exact nature of the reactive species was ambiguous (*e.g.*, “ $\text{BuOI}$ ”).<sup>[24,25]</sup> The carbonyl hypoiodite  $\text{CH}_3\text{CO}_2\text{I}$  has only been characterised in solution by  $^1\text{H}$  NMR spectroscopy and spectrophotometrically,<sup>[26,27]</sup> even though it has a proven track record as an *in situ* iodination reagent. Prior work on stabilised carbonyl hypoiodite ( $\text{O}–\text{I}–\text{N}$ ) complexes, which are hypoiodite complexes that could be isolated and characterised in the solid state, were first reported in the 1980s by Hartl *et al.*<sup>[28]</sup> However, they were then largely forgotten until the field was recently reinvigorated by the observation that the solid-state parameters of these neutral  $\text{O}–\text{I}–\text{N}$  complexes mimicked those of analogous  $[\text{N}–\text{I}–\text{N}]^+$  complexes (Figure 1),<sup>[29]</sup> suggesting that  $\text{O}–\text{I}–\text{N}$  com-

[a] M. Sc. V. Kolařík, Prof. Dr. K. Rissanen, Dr. J. S. Ward  
University of Jyväskylä  
Department of Chemistry  
40014 Jyväskylä, Finland  
E-mail: james.s.ward@jyu.fi

[b] M. Sc. V. Kolařík  
Department of Chemistry, Faculty of Technology  
Tomas Bata University in Zlín  
Vavrečkova 5669, 760 01 Zlín, Czech Republic

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**Figure 1.** The I–N bond lengths (in Å) of the iodine(I) complexes  $[\text{I}(\text{DMAP})_2]\text{PF}_6$  and  $\text{C}_6\text{H}_5\text{CO}_2\text{I}(\text{DMAP})$  showing their comparable values despite the difference of one of the coordinating ligands ( $\text{C}_6\text{H}_5\text{CO}_2$  vs.  $\text{DMAP}$ ).<sup>[14,29]</sup>

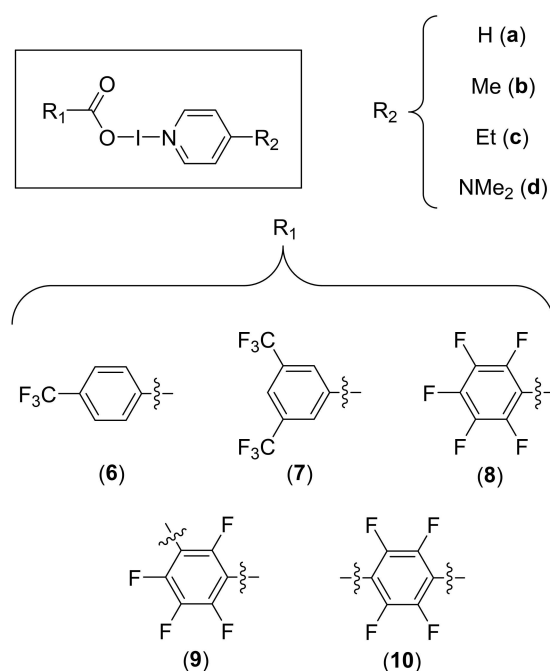
plexes could also be considered iodine(I) species. This renewed interest has rapidly expanded the solid-state examples of hypiodite complexes, which include *mono*, *bis*, and even *tris*(O—I–N) species,<sup>[29–31]</sup> as well as chiral carbonyl hypiodites derived from (*S*)-valine.<sup>[32]</sup> Despite their stabilisation, these isolable carbonyl hypiodites have been shown to act as iodine(I) reagents themselves,<sup>[33]</sup> potentially creating a new field of iodine(I) reagents that are intrinsically heteroleptic, a challenge encountered in the synthesis of monotopic-ligand [L—I–L]<sup>+</sup> halogen(I) complexes that suffer from ligand exchange in solution.<sup>[14,15,34,35]</sup>

Computational studies on the carbonyl hypiodite CF<sub>3</sub>CO<sub>2</sub>I–(DMAP) (DMAP = *N,N*-dimethylpyridin-4-amine) indicated that the F<sub>3</sub>CCO<sub>2</sub>I trifluorocarbonyl hypiodite was the strongest neutral halogen bond donor molecule, just surpassing that of *N*-iodosaccharin.<sup>[29]</sup> The formation of this pyridine-iodine(I) cation is proposed as the first step upon reaction of [I(py)<sub>2</sub>]<sup>+</sup> complexes,<sup>[36]</sup> and depending on which ligand more readily dissociates in O—I–N complexes, the formation of the same highly-reactive cation could be expected upon loss of the oxygen-donor ligand. These carbonyl, and most recently sulfonyl,<sup>[37]</sup> hypiodites currently provide the closest solid-state example of the elusive pyridine-iodine(I) cation, and therefore, the study of carbonyl hypiodites incorporating strongly electron-withdrawing substituents on a benzoyl skeleton offers new insights in this endeavour.

## Results and Discussion

The precursor silver(I) complexes silver(I) 4-(trifluoromethyl)benzoate (4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Ag; **1**), silver(I) 3,5-bis(trifluoromethyl)benzoate (3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>Ag; **2**), silver(I) 2,3,4,5,6-pentafluorobenzoate (C<sub>6</sub>F<sub>5</sub>CO<sub>2</sub>Ag; **3**),<sup>[38]</sup> silver(I) tetrafluoroisophthalate (1,3-(CO<sub>2</sub>Ag)<sub>2</sub>C<sub>6</sub>F<sub>4</sub>; **4**), and silver(I) tetrafluoroterephthalate (1,4-(CO<sub>2</sub>Ag)<sub>2</sub>C<sub>6</sub>F<sub>4</sub>; **5**) were synthesised from their respective carboxylic acids 4-(trifluoromethyl)benzoic acid, 3,5-bis(trifluoromethyl)benzoic acid, 2,3,4,5,6-pentafluorobenzoic acid, tetrafluoroisophthalic acid, and tetrafluoroterephthalic acid, respectively, in a straightforward one-pot synthesis first by deprotonation with NaOH to give the sodium salts, followed by cation exchange with AgNO<sub>3</sub>. The workups of **1–5** did show some variation from other silver(I) carboxylates in the literature due to their partial or good solubility in polar or organic solvents,<sup>[30–32]</sup> though were still isolated in reasonable yields (> 75%) except for **2**, for which no ideal combination of solvents could be found to separate the product from the side-products of the reaction.

The silver(I) precursor complexes (**1–5**), in combination with four different Lewis bases: pyridine (py; **a**), 4-methylpyridine (4-Mepy; **b**), 4-ethylpyridine (4-Etpy; **c**), *N,N*-dimethylpyridin-4-amine (DMAP; **d**), were utilised to synthesise the desired iodine(I) complexes **6a–d**, **7a–d**, **8a–d**, **9a–d**, and **10a/c**, respectively (Scheme 1). It should be noted that **10b** and **10d** could not be isolated in their pure forms, in solution or as solids, due to decomposition being observed when trying to concentrate/isolate them. Similarly, the silver(I) intermediates



**Scheme 1.** The numbering convention used for the carbonyl hypiodite complexes synthesised herein.

**1a–d**, **2a–d**, **4a–d**, and **5a–d** were not isolated due to their poor solubility in CH<sub>2</sub>Cl<sub>2</sub>. Nevertheless, the atypically soluble nature of **3** and its derivatives facilitated the isolation of **3a–d**, though **3d** was found to yield a product containing a 1:2 ratio of Ag:Ligand, even when using a 1:1 ratio in the reaction.

All of the reported hypiodite complexes, and the silver(I) intermediates **3a–d**, were investigated in solution via NMR studies (<sup>1</sup>H, <sup>19</sup>F, <sup>1</sup>H-<sup>15</sup>N HMBC). The <sup>1</sup>H NMR chemical shifts of the hypiodite complexes were found to follow the same trend of becoming more deshielded, as previously noted for other hypiodite complexes.<sup>[30–32]</sup> However, the <sup>1</sup>H NMR coordination shifts of the hypiodite complexes relative to their free Lewis bases were all modest, with shifts within the range of 0.24–0.42 (py/**6a–10a**), 0.13–0.17 (4-Mepy/**6b–9b**), 0.03–0.16 (4-Etpy/**6c–10c**), and 0.01–0.12 ppm (DMAP/**6d–9d**), with pyridine demonstrating the largest coordination shifts in general, and DMAP the smallest.

Despite the distance of the fluorine atoms from the O—I–N bond, the hypiodite complexes were investigated via <sup>19</sup>F NMR studies. The resulting <sup>19</sup>F NMR chemical shifts of the hypiodite complexes showed minimal differences within the series with observed ranges of 0.11 (**6a–d**), 0.06 (**7a–d**), ~1.5 (**8a–d**; though most values within 0.5 ppm), ~2.0 ppm (**9a–d**; though most values within 0.3 ppm), and 0.20 ppm (**10a/c**), revealing that <sup>19</sup>F NMR spectroscopy to be insensitive to the different Lewis bases utilised. Likewise, minimal differences were observed between the <sup>19</sup>F NMR chemical shifts of the silver(I) intermediates **3a–c** versus their respective hypiodite analogues **8a–c**, with differences between the pairs of complexes ranging from 0.48 to 2.35 ppm.

The  $^{15}\text{N}$  NMR chemical shifts, as determined by  $^1\text{H}$ - $^{15}\text{N}$  HMBC experiments, of the pyridinic nitrogen atoms in halogen(I) complexes have been previously shown to be the most characteristic indicator for the identification of hypiodite complexes.<sup>[29–32]</sup> These  $^1\text{H}$ - $^{15}\text{N}$  HMBC experiments were successfully performed on all isolated hypiodites reported herein (Table S1), and offer a rare opportunity to study the effect of Lewis basicity over a series of closely related carbonyl hypiodite halogen bond donors. The  $^{15}\text{N}$  NMR chemical shifts reveal that **6a–d** were observed to be the most deshielded out of all the Lewis bases screened, whilst **8a–d** were the most shielded, which can be attributed to being the least (**6**) and most (**8**) electron-withdrawing halogen bond donors. The differences in chemical shifts for a Lewis bases across different halogen bond donors were also minimal, demonstrating the predictive potential of such studies once a large enough library of data has been amassed.

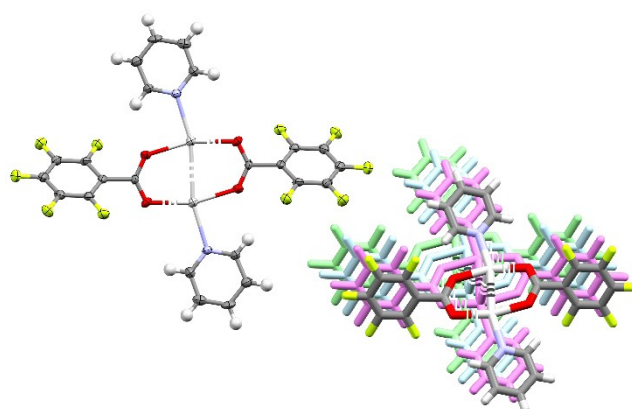
The coordination shift,  $\Delta\delta_{\text{N}}$ , is defined as the difference between the chemical shift of the pyridinic nitrogen atom in the uncoordinated ligand ( $\delta[^{15}\text{N}_{\text{Ligand}}]$ ) and the hypiodite complex ( $\delta[^{15}\text{N}_{\text{Hypiodite}}]$ ) incorporating that same ligand, often reported as a positive value, with large values of  $\Delta\delta_{\text{N}}$  previously being observed upon formation of the iodine(I) complexes relative to their uncoordinated ligands.<sup>[29]</sup> The free ligands (in  $\text{CD}_2\text{Cl}_2$ ) py ( $-67.7$  ppm),<sup>[14]</sup> 4-Mepy ( $-75.1$  ppm),<sup>[31]</sup> 4-Etpy ( $-75.6$  ppm),<sup>[30]</sup> and DMAP ( $-105.3$  ppm)<sup>[14]</sup> were found to demonstrate significant coordination shifts upon formation of the hypiodite complexes of 87.1–97.8 ppm for **6a–10a**, 90.6–101.6 ppm for **6b–9b**, 89.9–100.8 ppm for **6c–10c**, and 108.4–121.4 ppm for **6d–9d**. These relatively narrow ranges of  $\Delta\delta_{\text{N}}$  of 10.7 (py), 11.0 (4-Mepy), 10.9 (4-Etpy), and 13.0 ppm (DMAP) across the various benzoyl ligands indicate that strict electronic conditions are enforced by the iodine(I), despite variations of the benzoyl ligand.

The 1,2-*bis*(O–I–N) analogue of **9c** and **10c**, (tetrafluorophthaloyl-OI)(4-Etpy)<sub>2</sub>,<sup>[30]</sup> has also been reported previously now permitting the whole series of isomers (1,2-, 1,3-, and 1,4-substituted) of these tetrafluorophenylene dicarboxylate complexes to be compared. The 1,2-analogue was observed to have a  $^{15}\text{N}$  NMR chemical shift of  $-171.2$  ppm, with the 1,3- and 1,4-analogues having  $\delta_{\text{N}}$  values of  $-173.3$  and  $-175.4$  ppm, respectively, demonstrating a trend toward being more shielded going from 1,2- to 1,4-substitution. The differences in chemical shifts are also an identical incremental 2.1 ppm going from 1,2- to 1,3-substitution, and 1,3- to 1,4-substitution, indicating the potential to target desirable traits through rational design if libraries of such adaptations could be catalogued.

As a final note on the solution studies, the possibility of  $\text{H}_2\text{O}$  intolerance of the hypiodite complexes was tested through the preparation of **8a** under Schlenk conditions, and the subsequent NMR spectra recorded under an inert atmosphere in a Young's NMR tube using dry  $\text{CD}_2\text{Cl}_2$ . This gave a nearly identical value of  $-165.6$  ppm for the  $^{15}\text{N}$  NMR chemical shift compared to a separate sample previously recorded under ambient conditions in a non-treated  $\text{CD}_2\text{Cl}_2$  solvent (*cf.*  $-165.5$  ppm).

The silver(I) derivatives of carboxylates are usually quite insoluble with the exception of strongly polar solvents like dimethyl sulfoxide, which is unsurprising given their proclivity to form dimeric subunits that readily assemble in polymeric networks via  $\text{Ag}\cdots\text{Ag}$  and  $\text{Ag}\cdots\text{O}$  interactions.<sup>[31]</sup> This was similarly observed for the precursor **1**, for which the solid-state structure was obtained using dimethyl sulfoxide as the solvent. However, the greatly increased solubility of **3** permitted the isolation of its derivatives in the same organic solvent (dichloromethane) as the hypiodite complexes without decomposition. Complexes **3a** and **3b**, analogous to that observed previously for  $[\text{tBuCO}_2\text{Ag}(\text{DMAP})_2]_2$ ,<sup>[31]</sup> formed discrete dimeric subunits with the silver(I) atoms capped by the two py or 4-Mepy ligands, which in turn pack into 1D chains via bridging  $\text{Ag}\cdots\text{Ag}$  interactions of 3.0495(7) and 3.0196(3) Å for **3a** and **3b**, respectively (Figure 2). Complex **3c** possessed the same dimeric core of the **3**, but in contrast to **3a** and **3b**, the silver(I) was capped on each end by an additional pentafluorobenzoate bridging to a silver(I) centre connected to two 4-Etpy ligands. These inequivalent silver(I) centres formed a 1D chain via  $\text{Ag}\cdots\text{O}$  interactions to another identical fragment, though it should be noted that with the same 1:1 stoichiometry of Ag:Ligand. Complex **3d** could only be isolated as the DMAP adduct, **3d-DMAP** (*i.e.*, in a 1:2 Ag:Ligand ratio), even when a 1:1 stoichiometry was used. Whilst these silver(I) complexes only add to the already myriad examples of silver(I) chemistry, they are of relevance because they illustrate that the silver(I) to iodine(I) cation exchange process can proceed without issue via *non-2*-coordinate silver(I) centres, for which only a few examples currently exist.<sup>[31,39]</sup> This is in contrast to the larger field of  $[\text{N}-\text{X}-\text{N}]^+$  halogen(I) chemistry, where the 2-coordinate  $[\text{N}-\text{Ag}-\text{N}]^+$  complexes are routinely isolated,<sup>[14,16,40]</sup> leading to the erroneous supposition that a 2-coordinate silver(I) centre might be a prerequisite for the subsequent cation exchange reaction.

There are only a handful of prior solid-state examples of these stabilised carbonyl hypiodites complexes, totalling 22 to date.<sup>[21]</sup> Therefore, the 15 examples of O–I–N complexes



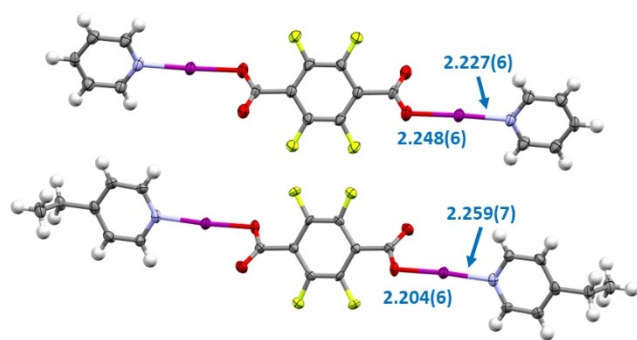
**Figure 2.** The dimeric subunit of **3a** in its solid-state structure (left; thermal ellipsoids at 50% probability), and the 1D chain formed via packing of four molecules of the dimeric subunit of **3a** (right; additional molecules block coloured for clarity).

contained herein represent a significant contribution, especially given the crystallographically complete series of **6–8** derivatives (*sans 7c*), which demonstrate systematic changes of both the oxygen- and nitrogen-bound ligands around the iodine(I) centre (Table 1). It should also be noted that prior solid-state examples of a 1,4-*bis*(O–I–N) motif had not been reported, which has now been achieved with derivatives of **10** (Figure 3).

Given the linear 2-coordinate nature of iodine(I) complexes and their propensity to exist within a relatively narrow range of bond lengths,<sup>[2]</sup> the distance between ligand donor atoms, *i.e.*,

Complex	<b>a</b> (py)	<b>b</b> (4-Mepy)	<b>c</b> (4-Etpy)	<b>d</b> (DMAP)
C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> I (Prior work) <sup>[28,29]</sup>	2.164(5)/ 2.296(7) <sup>[a]</sup>	–	–	2.210(3)/ 2.241(3)
<b>6</b> (4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> )	2.173(2)/ 2.283(3) <sup>[a]</sup>	2.195(3)/ 2.244(3)	2.182(5)/ 2.253(6)	2.244(4)/ 2.215(5)
<b>7</b> (3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> )	2.189(8)/ 2.236(10) <sup>[a]</sup>	2.192(5)/ 2.252(7)	<sup>[b]</sup>	2.229(3)/ 2.206(4)
<b>8</b> (C <sub>6</sub> F <sub>5</sub> CO <sub>2</sub> )	2.247(5)/ 2.221(6)	2.220(3)/ 2.245(3)	2.214(6)/ 2.219(7)	2.224(3)/ 2.221(4)
1,2-(CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> F <sub>4</sub> (Prior work) <sup>[30]</sup>	–	–	2.213(6)/ 2.208(6) 2.223(6)/ 2.233(6)	–
<b>9</b> (1,3-(CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> F <sub>4</sub> )	2.180(7)/ 2.27(1) <sup>[c]</sup>	2.190(4)/ 2.262(4) 2.199(4)/ 2.256(4)	<sup>[b]</sup>	<sup>[b]</sup>
<b>10</b> <sup>[d]</sup> (1,4-(CO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> F <sub>4</sub> )	2.248(6)/ 2.227(6)	<sup>[e]</sup>	2.204(6)/ 2.259(7)	<sup>[e]</sup>

[a] Average values reported due to multiple crystallographically independent molecules being present in the asymmetric unit cell. [b] Suitable quality crystals for SCXRD of **7c**, **9c**, and **9d** could not be obtained. [c] Values for second O–I–N group were omitted due to being disordered. [d] Derivatives of **10** all possessed pairs of symmetry equivalent O–I–N groups. [e] **10b** and **10d** were not isolated.



**Figure 3.** The solid-state structures of **10a** (top) and **10c** (bottom) annotated with their O–I and I–N bond lengths in Å (both complexes contain symmetry-equivalent O–I–N groups; thermal ellipsoids at 50% probability).

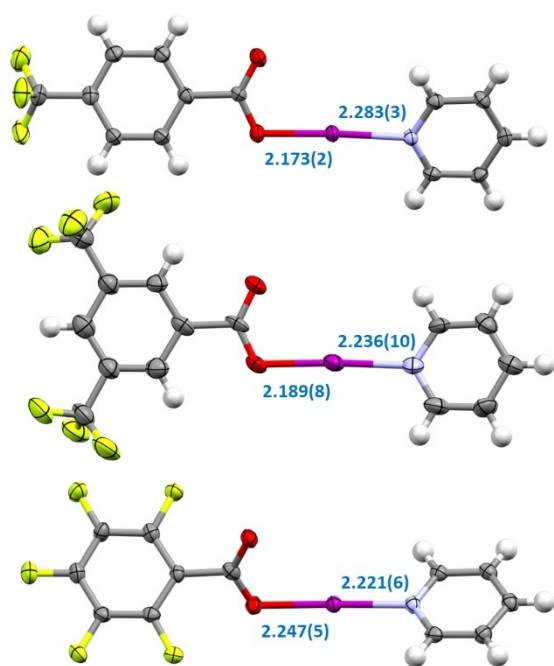
the coordinating nitrogen and oxygen donor atoms of the ligands contributing to the O–I–N motif, are reliably found to be ~4.45 Å apart.<sup>[21]</sup> Therefore, modification of the Lewis basicity of the ligands does not alter the aforementioned ~4.45 Å distance between the coordinating atoms, but rather skews the relative position of the iodine(I) centre between those coordinating atoms. This empirical observation was also found to hold true for hypiodites **6a–10c**, with the range of O···N intramolecular distances being between a minimum of 4.418 Å for **7a**, to a maximum of 4.475 Å for **10a**, though this does not account for any deviations from the ideal linear (180°) geometry of the iodine(I) centre. However, the deviations from this ideal geometry were minimal (with a maximum deviation of 7.5° for **7d**), and the hypiodite complexes giving rise to the aforementioned smallest (**7a**) and largest (**10a**) O···N intramolecular distances possessing O–I–N angles of 176.9(2)° and 177.5(2)°, respectively, which can be considered negligibly distorted from linearity.

The predicted trend of increasing Lewis basicity (from **a** to **d**) resulting in a shortening of the I–N bond, concomitant with the elongation of the O–I bond length, was found for derivatives of **6** and **7** (as **6b/6c** potentially overlap in their bond lengths once a 3σ error of the SCXRD measurement is accounted for). Similar remarks also hold true for the limited solid-state examples of derivatives of **9** and **10**.

Interestingly, the strongest electron-withdrawing benzoyl (**8**) was found to be almost entirely resistant to the differing Lewis basicities of **a–d**, with **8a/c/d** all having I–N bond lengths of ~2.22 Å, an apparent anomaly that has not previously been observed. Complex **8b** breaks from this observation with an I–N bond length of 2.245(3) Å, though it is only just outside a 3σ tolerance in comparison to the values of complexes **8a/c/d**. The O–I bond lengths of **8b–d** are similarly unresponsive to the Lewis basicity, with a variation of only 0.01 Å between them, this time with the value of complex **8a** (2.247(5) Å) only just lying beyond a 3σ tolerance. Nevertheless, these observations should be taken in context and care should be taken to avoid potentially *over*-analysing these crystallographic parameters, especially given that the six crystallographically independent molecules of **6a** also show a variation of 0.02 Å in their I–N bond lengths due to packing effects, some of which also lie outside a 3σ tolerance.

When comparing the different electron-withdrawing substituents of the benzoyl ligands in **6a–8a** (Figure 4), the trend of lengthening the O–I bond length from **6a** (2.168(2)–2.178(2) Å) to **8a** (2.247(5) Å) is apparent, concomitant with shortening of the respective I–N bonds. However, with increasing Lewis basicity this trend becomes less pronounced, with **6d–8d** having comparable values for both their O–I (2.244(4), 2.229(3), and 2.224(3) Å, respectively) and I–N (2.215(5), 2.206(4), and 2.221(4) Å, respectively) bond lengths, which can be attributed to the stronger Lewis basicity of DMAP (and also with 4-Mepy in **6b–8b**) surpassing the benzoyl substituents as the dominant influence with respect to the halogen bonding.

In relation to the original goal of isolating examples of increased pyridine-iodine(I) cation character through the use of



**Figure 4.** The solid-state structures of **6 a–8 a** (top to bottom) annotated with their O–I and I–N bond lengths in Å (for **6 a** and **7 a**, where multiple molecules were present in the asymmetric unit cell, average values are given; thermal ellipsoids at 50% probability).

strongly electron-withdrawing groups on the oxygen-donor ligands, *i.e.*, shorter I–N bond lengths in the hypoiodite complexes, this was only partially achieved. Indeed, the I–N bond lengths of **6 d**, **7 d**, and **8 a/c/d**, have noticeably reduced values of  $\sim 0.02$ – $0.04$  Å compared to their benzoyl derivatives ( $\text{C}_6\text{H}_5\text{CO}_2\text{I}(\text{py})$ ) and ( $\text{C}_6\text{F}_5\text{CO}_2\text{I}(\text{DMAP})$ ), which had I–N bond lengths of 2.292(6)/2.299(7) and 2.241(3) Å, respectively.<sup>[29]</sup> However, the complexes herein did not rival the more effective inducement of ‘pyridine-iodine(I) cation’ character observed for a trifluoroacetate derivative in  $\text{CF}_3\text{C}(\text{O})\text{OI}(\text{DMAP})$ , which had an I–N bond length of 2.173(4) Å. This was also reflected in the solution studies. When compared to the previously reported  $\text{C}_6\text{H}_5(\text{O})\text{OI}(\text{py})$  and  $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OI}(\text{DMAP})$  analogues which had  $^{15}\text{N}$  NMR chemical shifts of  $-148.7$  and  $-209.5$  ppm,<sup>[28,29]</sup> respectively, the **6 a–10 a** and **6 d–9 d** series were all more shielded comparatively, due to their strongly electron-withdrawing substituents on the oxygen-coordinated halogen bond acceptor. Nevertheless, the complexes herein did not surpass the more shielded  $\text{CF}_3\text{C}(\text{O})\text{OI}(\text{DMAP})$  at  $-238.0$  ppm.<sup>[29]</sup>

A recent study utilising sulfonates in place of the carboxylates has yielded analogous complexes with impressively shorter I–N bond lengths (*cf.*  $\sim 2.14$  Å).<sup>[37]</sup> However, these (S)O–I–N iodine(I) sulfonate complexes necessitated being kinetically trapped at low temperatures, without which, they were observed to decompose rapidly within seconds. As such, (S)O–I–N complexes are ultimately an unattractive prospect with respect toward further studies, for example as potential halogenation reagents, in comparison to carbonyl hypoiodites.

## Conclusions

In conclusion, a variety of carbonyl hypoiodite complexes were prepared from fluorine-substituted analogues of benzoate and 4-substituted pyridines, and synthesised via their respective silver(I) precursors. The atypically good solubility of **3** allowed its intermediates (**3 a–d**) to be isolated in the solid state from the same solvent as the subsequent hypoiodite derivatives (**8 a–d**), providing strong evidence that the silver(I) to iodine(I) cation exchange reaction does not require 2-coordinate silver(I) complexes to proceed. Carbonyl hypoiodite complexes incorporating strongly electron-withdrawing substituents were prepared to explore the possibility of inducing increased ‘pyridine-iodine(I) cation’ character, observed via a shortening of the I–N bond lengths (concomitant with lengthening of the O–I bonds). Solid-state observations confirmed significant shortening of the I–N bond lengths for derivatives of **7** and **8** (*cf.* **7 d**, **8 a/c/d**), though not to the same extent as the prior literature examples based on trifluoroacetate. Nonetheless, the hypoiodite complexes reported herein represent the largest single contribution to the field, a confirmation that electron-withdrawing substituents on the oxygen-donor ligand can yield hypoiodite complexes more amenable to solid-state studies, and as a result contains several complete systematically-varied series of structurally-isolated hypoiodite complexes. The solid-state studies are supported by extensive solution studies, which permitted further detailed comparisons to be drawn for these systematically-varied series of hypoiodites.

## Supporting Information

The authors have cited additional references within the Supporting Information Ref. [41–43]).

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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- [1] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **2016**, *116*, 2478–2601.
- [2] J. S. Ward, K.-N. Truong, M. Erdélyi, K. Rissanen, in *Compr. Inorg. Chem. III* (Eds.: J. Reedijk, K. R. B. T. Poepelmeier), Elsevier, Oxford, **2023**, pp. 586–601.
- [3] T. Clark, M. Hennemann, J. S. Murray, P. Politzer, *J. Mol. Model.* **2007**, *13*, 291–296.
- [4] J. Pancholi, P. D. Beer, *Coord. Chem. Rev.* **2020**, *416*, 213281.
- [5] M. H. Kolář, P. Hobza, *Chem. Rev.* **2016**, *116*, 5155–5187.
- [6] L. Turunen, U. Warzok, R. Puttreddy, N. K. Beyeh, C. A. Schalley, K. Rissanen, *Angew. Chem. Int. Ed.* **2016**, *55*, 14033–14036.
- [7] L. Turunen, A. Peuronen, S. Forsblom, E. Kalenius, M. Lahtinen, K. Rissanen, *Chem. A Eur. J.* **2017**, *23*, 11714–11718.
- [8] A. Vanderkooy, A. K. Gupta, T. Földes, S. Lindblad, A. Orthaber, I. Pápai, M. Erdélyi, *Angew. Chem. Int. Ed.* **2019**, *58*, 9012–9016.
- [9] E. Taipale, J. S. Ward, G. Fiorini, D. L. Stares, C. A. Schalley, K. Rissanen, *Inorg. Chem. Front.* **2022**, *9*, 2231–2239.
- [10] C. Schumacher, K.-N. Truong, J. S. Ward, R. Puttreddy, A. Rajala, E. Lassila, C. Bolm, K. Rissanen, *Org. Chem. Front.* **2024**, *11*, 781–795.
- [11] G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati, K. Rissanen, *Pure Appl. Chem.* **2013**, *85*, 1711–1713.
- [12] M. Bedin, A. Karim, M. Reitti, A.-C. C. Carlsson, F. Topić, M. Cetina, F. Pan, V. Havel, F. Al-Ameri, V. Sindelar, et al., *Chem. Sci.* **2015**, *6*, 3746–3756.
- [13] A.-C. C. Carlsson, K. Mehmeti, M. Uhrbom, A. Karim, M. Bedin, R. Puttreddy, R. Kleinmaier, A. A. Neverov, B. Nekouishahraki, J. Gräfenstein, et al., *J. Am. Chem. Soc.* **2016**, *138*, 9853–9863.
- [14] J. S. Ward, G. Fiorini, A. Frontera, K. Rissanen, *Chem. Commun.* **2020**, *56*, 8428–8431.
- [15] S. Yu, J. S. Ward, *Dalton Trans.* **2022**, *51*, 4668–4674.
- [16] J. S. Ward, *CrystEngComm* **2022**, *24*, 7029–7033.
- [17] J. Barluenga, J. M. González, P. J. Campos, G. Asensio, *Angew. Chem. Int. Ed.* **1985**, *24*, 319–320.
- [18] J. Barluenga, J. M. González, M. A. García-Martin, P. J. Campos, G. Asensio, *J. Chem. Soc., Chem. Commun.* **1992**, 1016–1017.
- [19] J. Ezquerro, C. Pedregal, C. Lamas, J. Barluenga, M. Pérez, M. A. García-Martin, J. M. González, *J. Org. Chem.* **1996**, *61*, 5804–5812.
- [20] G. Espuña, G. Arsequell, G. Valencia, J. Barluenga, M. Pérez, J. M. González, *Chem. Commun.* **2000**, 1307–1308.
- [21] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr. Sect. B* **2016**, *72*, 171–179.
- [22] P. Pröhm, W. Berg, S. M. Rupf, C. Müller, S. Riedel, *Chem. Sci.* **2023**, *14*, 2325–2329.
- [23] R. Kawasumi, S. Narita, K. Miyamoto, K. Tominaga, R. Takita, M. Uchiyama, *Sci. Rep.* **2017**, *7*, 17967.
- [24] D. D. Tanner, G. C. Gidley, N. Das, J. E. Rowe, A. Potter, *J. Am. Chem. Soc.* **1984**, *106*, 5261–5267.
- [25] R. Montoro, T. Wirth, *Org. Lett.* **2003**, *5*, 4729–4731.
- [26] J. L. Courtneidge, J. Luszyk, D. Pagé, *Tetrahedron Lett.* **1994**, *35*, 1003–1006.
- [27] T. Hokamp, A. T. Storm, M. Yusubov, T. Wirth, *Synlett* **2018**, *29*, 415–418.
- [28] H. Hartl, M. Hedrich, *Z. Naturforsch. B* **1981**, *36b*, 922–928.
- [29] S. Yu, J. S. Ward, K.-N. Truong, K. Rissanen, *Angew. Chem. Int. Ed.* **2021**, *60*, 20739–20743.
- [30] E. Kramer, S. Yu, J. S. Ward, K. Rissanen, *Dalton Trans.* **2021**, *50*, 14990–14993.
- [31] J. S. Ward, J. Martõnova, L. M. E. Wilson, E. Kramer, R. Aav, K. Rissanen, *Dalton Trans.* **2022**, *51*, 14646–14653.
- [32] M. Mattila, K. Rissanen, J. S. Ward, *Chem. Commun.* **2023**, *59*, 4648–4651.
- [33] L. M. E. Wilson, K. Rissanen, J. S. Ward, *New J. Chem.* **2023**, *47*, 2978–2982.
- [34] D. von der Heiden, K. Rissanen, M. Erdélyi, *Chem. Commun.* **2020**, *56*, 14431–14434.
- [35] S. Yu, E. Kalenius, A. Frontera, K. Rissanen, *Chem. Commun.* **2021**, *57*, 12464–12467.
- [36] D. von der Heiden, F. B. Németh, M. Andreasson, D. Sethio, I. Pápai, M. Erdélyi, *Org. Biomol. Chem.* **2021**, *19*, 8307–8323.
- [37] R. Puttreddy, P. Kumar, K. Rissanen, *Chem. A Eur. J.* **2024**, e202304178.
- [38] P. Sartori, M. Weidenbruch, *Chem. Ber.* **1967**, *100*, 3016–3023.
- [39] J. S. Ward, A. Frontera, K. Rissanen, *Inorg. Chem.* **2021**, *60*, 5383–5390.
- [40] J. S. Ward, R. M. Gomila, A. Frontera, K. Rissanen, *RSC Adv.* **2022**, *12*, 8674–8682.
- [41] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8.
- [42] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [43] G. M. Sheldrick, *Acta Crystallogr. Sect. C, Struct. Chem.* **2015**, *71*, 3–8.
- [44] Deposition numbers 2328627 (for **1**), 2328628–2328631 (for **3a–d**), 2328632–2328635 (for **6a–6d**), 2328636–2328638 (for **7a/b/d**), 2328639–2328642 (for **8a–8d**), 2328643–2328644 (for **9a/9b**), and 2328645–2328646 (for **10a/10c**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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