



## O–I–O halogen bond of halonium ions†

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**The reactivity of halonium ions is conveniently modulated by three-center, four-electron halogen bonds. Such stabilized halonium complexes are valuable reagents for oxidations and halofunctionalization reactions. We report the first example of the stabilization of a halonium ion in a three-center, four-electron halogen bond with two oxygen ligands. The influence of electron density and solvent on the stability of the complexes is assessed. O–I–O halogen bond complexes are applicable as synthetic reagents and as supramolecular synthons.**

A halogen bond is the attractive interaction of an electrophilic area of a halogen with a nucleophile.<sup>1</sup> It was first observed in 1863 by Guthrie,<sup>2</sup> but only began to receive significant attention towards the end of the 20th century. Today, halogen bonding is one of the fastest growing research topics in chemistry<sup>3</sup> with applications for example in crystal engineering,<sup>4,5</sup> drug design,<sup>6–9</sup> material sciences,<sup>10–12</sup> and organic synthesis.<sup>13–15</sup>

A halonium ion<sup>16</sup> (X<sup>+</sup>) has an electron depleted p-orbital that can interact simultaneously with two Lewis bases, forming a linear three-center, four-electron (3c4e) halogen bond.<sup>17</sup> Due to their electron deficiency, halonium ions are strong halogen bond donors. The energy range of halogen bonds overlaps with that of hydrogen bonds,<sup>18</sup> with the 3c4e halogen bonds being among the strongest secondary interactions (up to 120 kJ mol<sup>−1</sup>).<sup>17</sup> In addition to the 3c4e bonds<sup>19</sup> in trihalide anions,<sup>20</sup> 3c4e halogen bond complexes have previously been formed using nitrogen,<sup>21–23</sup> sulphur,<sup>24–26</sup> selenium,<sup>27,28</sup> tellurium,<sup>29</sup> and mixed nitrogen and oxygen electron donors<sup>30–32</sup> (Fig. S1, ESI†). Similarly to analogous short, strong hydrogen bonds (SSHB), which are of interest for stabilizing reaction intermediates and transition states,<sup>33,34</sup> 3c4e

halogen bond complexes are applicable as synthetic reagents and in the design of complex supramolecular structures.<sup>17,26,35–39</sup>

We report herein the first [O–I–O]<sup>+</sup>-type 3c4e halogen bond complexes, employing two oxygen donor ligands for the stabilization of a reactive halonium ion. This is significant as investigations of halogen bonding applying oxygen ligands as Lewis bases have been scarce,<sup>40</sup> and 3c4e halogen bonding with two oxygen ligands has so far been scarcely explored.<sup>17,51</sup> Our study provides new insights into both halogen bonding and 3c4e bonds. Additionally, [O–I–O]<sup>+</sup> complexes are of interest for the development of new supramolecular synthons and of improved reagents for halofunctionalization and oxidation reactions.

Due to the formal negative charge on the oxygen, we anticipated pyridyl *N*-oxides to be suitable Lewis bases for the formation of an [O–I–O]<sup>+</sup> 3c4e halogen bond. The complex (**1-OMe**)<sub>2</sub>-**I** (Fig. 1 and Table 1) was synthesized from the electron rich 4-methoxy pyridine *N*-oxide (**1-OMe**) following a protocol previously applied for the generation of the analogous [N–I–N]<sup>+</sup> halogen bond complexes<sup>23</sup> (ESI†). Formation of the 3c4e halogen bond was confirmed by the −31.2 ppm <sup>15</sup>N NMR coordination shift in dry CD<sub>3</sub>CN, as detected on the nitrogen of the **1-OMe** ligand ( $\delta^{15}\text{N}_{\text{coord}} = \delta^{15}\text{N}_{\text{complex}} - \delta^{15}\text{N}_{\text{ligand}}$ , Table 1).

This  $\delta^{15}\text{N}_{\text{coord}}$  is in reasonable agreement with that predicted by DFT, and is significantly smaller than that of the analogous [N–I–N]<sup>+</sup> complex of iodine(i) formed with pyridine ((**Py**)<sub>2</sub>-**I**,  $\delta^{15}\text{N}_{\text{coord}} = -109.0$  ppm).<sup>41</sup> Computations predict the (**1-OMe**)<sub>2</sub>-**I** complex to be slightly more stable than (**Py**)<sub>2</sub>-**I** ( $\Delta G_{\text{rel}} = -2.7$  kcal mol<sup>−1</sup>, Table 1). The smaller  $|\delta^{15}\text{N}_{\text{coord}}|$  yet larger stability of (**1-OMe**)<sub>2</sub>-**I** as compared to (**Py**)<sub>2</sub>-**I** is not a contradiction because the iodine(i) of the former complex does not coordinate directly to the nitrogen but to the *N*-oxide oxygen. The larger  $|\delta^{15}\text{N}_{\text{coord}}|$  of (**1-OMe**)<sub>2</sub>-**I** as compared to (**1-OMe**)<sub>2</sub>-**Ag** ( $\delta^{15}\text{N}_{\text{coord}} = -2.1$  ppm, Fig. 1 and Table 1) is explained by CD<sub>3</sub>CN coordination to silver(i) but not to the iodine(i) of the 3c4e complex (Fig. S77, ESI†).<sup>42,43</sup> A previous study of silver(i) pyridine-*N*-oxide complexes reported the formation of various coordination complexes, such as [(**Py**)<sub>2</sub>-**O**]-**Ag**[(NO<sub>3</sub>)<sub>3</sub>],

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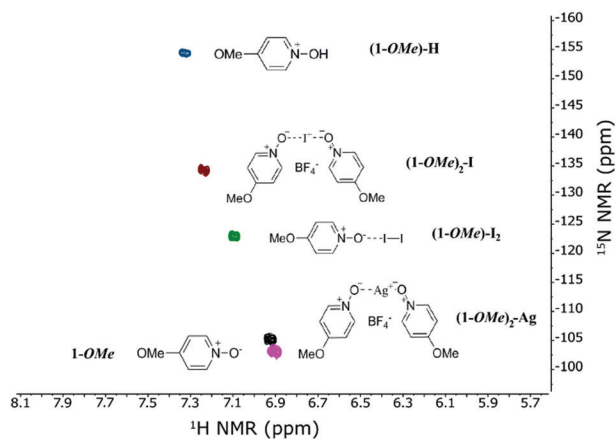


Fig. 1 The  $^{15}\text{N}$  NMR chemical shifts of 4-methoxypyridine *N*-oxide (**1-OMe**, pink) and of its silver(i) (black, (**1-OMe**)<sub>2</sub>-Ag), iodine (green, (**1-OMe**)<sub>2</sub>-I<sub>2</sub>), iodine(i) (red, (**1-OMe**)<sub>2</sub>-I) and proton (blue, (**1-OMe**)-H) complexes were acquired by  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC NMR ( $\text{CD}_3\text{CN}$ , 500/51 MHz), with detection on the proton meta to the pyridine nitrogen (H-3) of the complexes.

[[Py-O]<sub>2</sub>-Ag](OMs), [[Py-O]<sub>3</sub>-Ag](OTf<sub>2</sub>N), [[Py-O]<sub>3</sub>-Ag](OTf), [[Py-O]<sub>8</sub>-Ag<sub>3</sub>](OTf)<sub>3</sub> in the solid state.<sup>44</sup> This further confirms that silver(i) may form multicoordinate species. (**1-OMe**)<sub>2</sub>-Ag is likely in a ligand exchange equilibrium with  $\text{CD}_3\text{CN}$   $\Delta G < 2 \text{ kcal mol}^{-1}$ , (Table S3, ESI<sup>†</sup>), which explains the deviation of the small  $|\delta^{15}\text{N}_{\text{coord}}|$  of (**1-OMe**)<sub>2</sub>-Ag from the value predicted by DFT (Table 1 and Fig. S77, ESI<sup>†</sup>). Hence, in contrast to  $[\text{N-Ag-N}]^+$  complexes,<sup>42</sup> the  $[\text{O-Ag-O}]^+$  complex (**1-OMe**)<sub>2</sub>-Ag is to a large extent dissociated in  $\text{CD}_3\text{CN}$ . Upon mixing **1-OMe** with iodine in  $\text{CD}_3\text{CN}$ , at the same concentrations as used to form (**1-OMe**)<sub>2</sub>-I, the coordination shift was consistent with the formation of a weak,

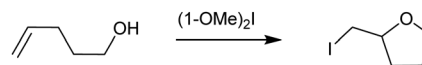


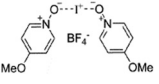
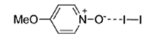
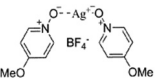
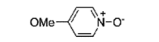
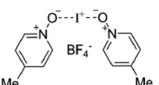
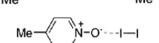
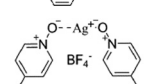
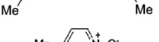
Fig. 2 Complex (**1-OMe**)<sub>2</sub>-I was applicable as a halonium transfer reagent for the iodocyclization of 4-penten-1-ol (see the ESI<sup>†</sup> for details).

conventional **1-OMe** · **I**<sub>2</sub> halogen bond ( $\delta^{15}\text{N}_{\text{coord}} = -11.4 \text{ ppm}$ ), which is also supported by the computed exergonicity of association ( $\Delta G_{\text{rel}} = -2.0 \text{ kcal mol}^{-1}$ ). Although the coordination shift is not necessarily a quantitative indicator for bond strength,<sup>41</sup> the 63% smaller  $|\delta^{15}\text{N}_{\text{coord}}|$  of **1-OMe** · **I**<sub>2</sub> as compared to (**1-OMe**)<sub>2</sub>-I is a qualitative reflection of the relative strengths of the conventional and the 3c4e halogen bonds with the same Lewis base, **1-OMe**.

The complex (**1-OMe**)<sub>2</sub>-I was applicable for iodocyclization of 4-penten-1-ol to form 2-(iodomethyl)tetrahydrofuran, with a comparable reaction rate to Barluenga's reagent, [bis(pyridine)-iodine(i)]<sup>+</sup> BF<sub>4</sub><sup>-</sup>, indicating the potential applicability of  $[\text{O-I-O}]^+$  3c4e halogen bond complexes as synthetic reagents (Fig. 2).<sup>38</sup> This suggestion is corroborated by the higher stability of (**1-OMe**)<sub>2</sub>-I as compared to Barluenga's reagent<sup>13,14</sup> ( $\Delta G_{\text{rel}}$ , Table 1), as calculated by DFT. A higher stability may result in improved reaction control and simpler reagent storage, for example.

The somewhat less electron rich **1-Me** ligand also provided a 3c4e halogen bond complex, (**1-Me**)<sub>2</sub>-I in dry  $\text{CD}_2\text{Cl}_2$ , with its formation being indicated by the observation of  $\delta^{15}\text{N}_{\text{coord}} = -27.7 \text{ ppm}$  (Table 1). This complex was applicable as halonium transfer reagent in the halocyclization of 4-penten-1-ol, similar to (**1-OMe**)<sub>2</sub>-I (Fig. 2). When forming (**1-Me**)<sub>2</sub>-I in  $\text{CD}_3\text{CN}$ , we observed some hydrolysis yielding **1-Me-H**, *i.e.* protonated *N*-oxide (Fig. S47–S52, ESI<sup>†</sup>). This is explained by the higher residual

Table 1 The  $^{15}\text{N}$  chemical shifts, calculated relative stabilities, bond distances and angles in complexes formed with ligands **1-OMe** and **1-Me**

| Structure   | $\delta^{15}\text{N}^a$ (ppm)            | $\delta^{15}\text{N}_{\text{calc}}^d$ (ppm) | $\Delta G_{\text{rel}}^e$ (kcal mol <sup>-1</sup> ) | $r(\text{O-X})^f$ [Å] | $\sigma(\text{N-O-X})^g$ [°] |
|---|--|---|---|-----------------------|------------------------------|
|  | -134.2 <sup>b</sup>                      | -143.5                                      | -2.7  | 2.22                  | 114.0                        |
|  | -122.8 <sup>b</sup>                      | -136.5                                      | -2.0  | 2.36                  | 112.9                        |
|  | -105.1 <sup>b</sup>                      | -131.4                                      | 4.5   | 2.12                  | 119.3                        |
|  | -103.0 <sup>b</sup>                      | -98.8                                       |   |                       |                              |
|  | -121.2, <sup>b</sup> -119.4 <sup>c</sup> | -129.0                                      | 1.9   | 2.22                  | 113.5                        |
|  | -102.2, <sup>b</sup> -98.9 <sup>c</sup>  | -120.1                                      | -0.4  | 2.39                  | 112.7                        |
|  | -92.0 <sup>b</sup>                       | -116.6                                      | 7.8   | 2.12                  | 124.5                        |
|  | -91.7, <sup>b</sup> -92.1 <sup>c</sup>   | -86.6                                       |   |                       |                              |

<sup>a</sup> Measured by  $^1\text{H}$ ,  $^{15}\text{N}$  HMBC. <sup>b</sup> Measured in  $\text{CD}_3\text{CN}$ . <sup>c</sup> Measured in  $\text{CD}_2\text{Cl}_2$ . <sup>d</sup> Computed using DFT with MeCN as solvent. <sup>e</sup> Relative stabilities of (OR)<sub>2</sub>-X (X = I, Ag) and (OR) · **I**<sub>2</sub> complexes are defined as Gibbs free energies of reactions  $[\text{Py-X-Py}]^+ + 2\text{OR} \rightarrow [\text{RO-X-OR}]^+ + 2\text{Py}$  and  $\text{OR} + \text{I}_2 \rightarrow \text{RO} \cdot \text{I}_2$ , respectively. <sup>f</sup> Computed O-Ag and O-I bond distances. <sup>g</sup> Computed N-O-Ag and N-O-I bond angles, see the ESI for computational details.



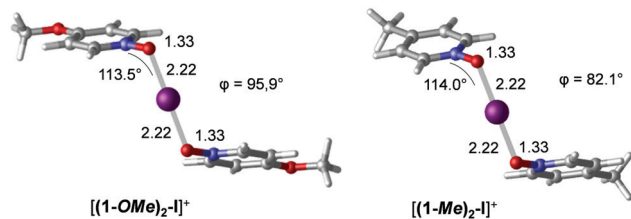


Fig. 3 Computationally optimized structures of the iodonium complexes with **1-OMe** and **1-Me**. Structures were optimized by DFT at  $\omega$ B97X-D/Def2SVP level. For details on the negligible influence of the  $\text{BF}_4^-$  counterion, see the ESI<sup>†</sup> and ref. 43. Selected bond distances are in Å, bond angles in degrees ( $\varphi$  refers to dihedral angle N–O...O–N).

water content of acetonitrile as compared to dichloromethane,<sup>45</sup> unlikely to be a consequence of different solvent polarities.<sup>46</sup> The **(1-Me)<sub>2</sub>I** and **(1-OMe)<sub>2</sub>I** complexes were stable at room temperature in solution under dry conditions, yet showed a larger moisture sensitivity than the corresponding [bis(pyridine)iodine(i)]<sup>+</sup>-type N–I–N halogen bond complexes.<sup>46,47</sup>

Attempts to form an [O–I–O]<sup>+</sup> halogen bond complex with dibenzofuran, a weaker Lewis base, did not succeed (Fig. S63–S67, ESI<sup>†</sup>). This was reflected by the lack of silver iodide precipitation upon addition of  $\text{AgBF}_4$  and  $\text{I}_2$  to the acetonitrile solution of dibenzofuran, the lack of <sup>1</sup>H NMR chemical shift changes throughout the experiment, and the DFT predicted instability of the corresponding iodine(i) complex (see the ESI<sup>†</sup> for details). This observation accentuates the importance of the identity of the Lewis base in the formation of stable halogen bond complexes.

The DFT optimized geometries of **(1-OMe)<sub>2</sub>I**<sup>+</sup> and **(1-Me)<sub>2</sub>I**<sup>+</sup> cations, shown in Fig. 3, possess the expected linear [O–I–O]<sup>+</sup> halogen bonds. It should be emphasized that the overall geometry vastly differs from the linear [N–I–N]<sup>+</sup> complexes formed by 4-methoxy- and 4-methylpyridine.<sup>41</sup> The overall bent geometries present opportunities for constructing alternate supramolecular architectures when using [O–X–O]<sup>+</sup> 3c4e complexes of pyridine *N*-oxides, as compared to the [N–X–N]<sup>+</sup> complexes formed by the corresponding pyridines.

Rotation about the O–I–O halogen bonds is practically free, as indicated by the marginal energy barrier, less than 0.3 kcal mol<sup>−1</sup>, predicted with DFT. The calculated O–I bonds show 37.2% shortening of the distance of the involved atoms as compared to the sum of their van der Waals radii ( $R_{\text{XB}} = 0.628$ , Bondi's radii,<sup>48,49</sup> Table 1).<sup>17</sup> This is comparable to the previously reported  $R_{\text{XB}} = 0.612$ – $0.654$  of the analogous [N–I–N]<sup>+</sup> complexes,<sup>22,41,45,50</sup> and the  $R_{\text{XB}} = 0.662$  of the [N–I–O]<sup>−</sup> halogen bond complexes (I–O distance 2.316 Å).<sup>30</sup> This further supports the formation of true 3c4e bonds<sup>17,22</sup> for **(1-OMe)<sub>2</sub>I** and **(1-Me)<sub>2</sub>I**.

In conclusion, we report the first examples of 3c4e [O–X–O]<sup>+</sup> halogen bond complexes. *N*-Oxides are shown to be privileged oxygen-donor ligands, as no such complex could be observed using an ether as Lewis base. Our data demonstrates the immense impact of the electron density of the electron donor on halogen bonding, with a 4.6 kcal mol<sup>−1</sup> relative stability decrease predicted upon a methoxy to methyl substitution, which was confirmed experimentally by the lower stability of **(1-Me)<sub>2</sub>I**, in contrast to **(1-OMe)<sub>2</sub>I**, in CD<sub>3</sub>CN. The higher

stability of **(1-Me)<sub>2</sub>I** in CD<sub>2</sub>Cl<sub>2</sub> as compared to CD<sub>3</sub>CN further reveals the importance of the solvent in the preparation of stabilized halonium complexes. This is of significance as Barluenga's reagent, for instance, was shown to be more reactive in CD<sub>3</sub>CN as compared to CD<sub>2</sub>Cl<sub>2</sub>.<sup>14</sup> The overall bent geometry of these complexes makes the [O–I–O]<sup>+</sup> bond a potential synthon that will result in different supramolecular architectures than those formed by the [N–I–N]<sup>+</sup> complexes of analogous pyridines. Furthermore, the reported [O–I–O]<sup>+</sup> halogen bond complexes are proven to be applicable as synthetic reagents, and are expected to be of interest in the development of future oxidation and halofunctionalization reagents. Introducing the [O–X–O]<sup>+</sup> motif, this work expands the scope of ligands known to be competent in the formation of 3c4e halogen bond complexes. Their further studies will provide novel fundamental insights into both the halogen bond and the 3c4e bonding phenomena.

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## Conflicts of interest

There are no conflicts to declare.

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