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Author(s): Yu, Shilin; Rissanen, Kari; Ward, Jas S.

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Mono- and Bis-Carbonyl Hypoiodites of the Tertiary Amines Quinuclidine and DABCO

Shilin Yu, Kari Rissanen,* and Jas S. Ward*

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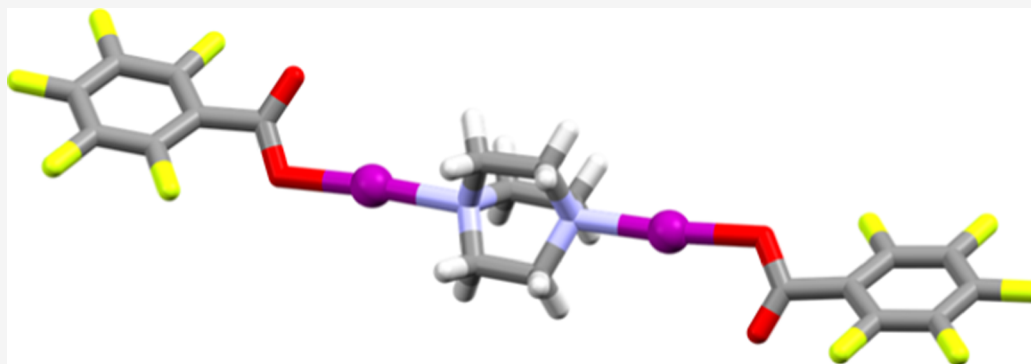
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ABSTRACT: Mono- and bis-carbonyl hypoiodites incorporating the tertiary amines quinuclidine (**1a–e**) or 1,4-diazabicyclo[2.2.2]octane (DABCO; **2a**, **2b**, and **2e**), respectively, have been synthesized and represent the first examples of hypoiodites stabilized by alkyl amines rather than aromatic Lewis bases (e.g., pyridine derivatives). These highly reactive complexes have been characterized in the solid state by SCXRD and DFT calculations. The DABCO hypoiodite derivatives are rare examples of ditopic bis(O–I–N) complexes and were found to display unexpected bonding parameters relative to iodine(I) complexes in which the DABCO is coordinating in a monotopic manner.

INTRODUCTION

The field of halogen bonding has continued to captivate and expand due to its utility as a noncovalent interaction in a myriad of applications that include the generation of porous, magnetic, and phosphorescent functional materials.^{1,2} Halogen bonding is defined as the interaction between the electrophilic region of a halogen atom (the halogen bond *donor*) and a neutral or anionic nucleophile (the halogen bond *acceptor*) and has advantages owing to its high-degree of linear directionality, a consequence of its origin as a σ -hole interaction,³ that has been deftly employed in self-assembling processes to create various supramolecular architectures.^{4–9}

Alkyl hypoiodites of the form R–OI (R = alkyl) have an established history of being used as iodinating reagents,^{10,11} though their in situ preparation and high reactivity have traditionally prohibited their definitive characterization as hypoiodites, with their exact identity still being a matter of debate (cf. “BuOI”).^{12,13} However, the structurally similar carbonyl hypoiodites, e.g., acetyl hypoiodite (also referred to as iodine monoacetate), $\text{CH}_3\text{C}(\text{O})\text{OI}$, are commonly *in situ*-generated iodination reagents, though they have only been characterized spectrophotometrically and by ¹H NMR spectroscopy.^{14,15}

In contrast, stabilized charge-neutral carbonyl hypoiodites containing an O–I–N motif of the form $\text{RC}(\text{O})\text{O–I–L}$

(where L = nitrogen-donor Lewis base) have recently reinvigorated the study of hypoiodites thanks to their isolation and characterization in the solid state,^{16–19} permitting structure–reactivity relationships to be established. These solid-state studies enabled their description as noncharged iodine(I) complexes not only based on structural comparisons to analogous cationic $[\text{N–I–N}]^+$ iodine(I) complexes^{20,21} but also through their ability to act as iodination reagents.²² The charge-neutral O–I–N hypoiodites are also reminiscent of their cationic $[\text{N–I–N}]^+$ counterparts in terms of their formation, with both types of complexes being reliably synthesized via cation exchange of their respective silver(I) analogues (Scheme 1).^{23–28} However, it is the differences between $[\text{N–I–N}]^+$ Barluenga-type and O–I–N hypoiodite complexes that hold the most potential.

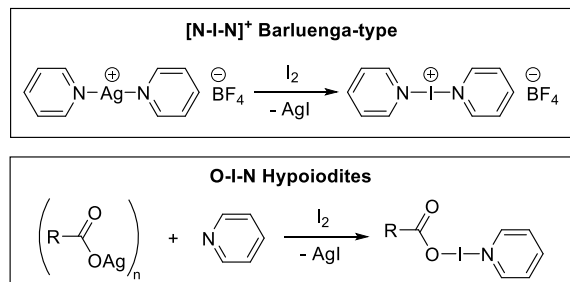
Historically, the $[\text{N–I–N}]^+$ iodine(I) complexes have overwhelmingly existed as homoleptic species incorporating

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Scheme 1. General Reaction Scheme to Prepare Iodine(I) Complexes, Using Pyridine as an Example of the Stabilizing Lewis Base, from Their Respective Silver(I) Precursors via Cation Exchange with Elemental Iodine



aromatic Lewis bases,^{9,20,23,24,29–31} i.e., $[L1-I-L1]^+$ ($L =$ Lewis base), including the eponymous Barluenga's reagent $[py-I-py]BF_4$ ($py =$ pyridine).³² While a few examples of heteroleptic, $[L1-I-L2]^+$, iodine(I) complexes do exist in the solid state,^{33,34} these have been found to be susceptible to ligand scrambling in solution, often resulting in mixtures also containing the disproportionation products $[L1-I-L1]^+$ and $[L2-I-L2]^+$,^{33,35} though recently this problem has been deftly side-stepped for pairs of monotopic ligands via the inducement of axial chirality in homoleptic complexes.³⁶ On the other hand, hypoiodites of the form the $RC(O)O-I-L$ are inherently heteroleptic in their substituents, offering a greater variety of options for modifying their substituents and ultimately tuning their properties, such as the first chiral hypoiodite complexes being recently reported based on chiral N -protected amino acids.³⁷

A handful of examples of $[N-I-N]^+$ iodine(I) complexes incorporating tertiary amines as the Lewis base have been synthesized,⁸ though only the bicyclic tertiary amines quinuclidine (quin),^{39–41} 1,4-diazabicyclo[2.2.2]octane (DABCO),^{34,42} and hexamethylenetetramine (HMTA)⁴³ have been structurally characterized due to their relative stability in comparison to their acyclic counterparts.⁴⁰ To date, the solid-state examples of $O-I-N$ hypoiodite complexes are limited to incorporating aromatic nitrogen-donor atom heterocycles and carboxylic acid derivatives.^{16–19} With no prior examples of $O-I-N$ hypoiodite complexes incorporating tertiary amines present in the literature, their synthesis and study are of great interest, given their potential to act as highly reactive iodination reagents.

RESULTS AND DISCUSSION

The quinuclidine (quin) carbonyl hypoiodites complexes $RC(O)O-I-quin$, where $R =$ ^tBu (**1a**), CF_3 (**1b**), $C_6H_4NO_2-4$ (**1c**), C_6H_4Br-4 (**1d**), and C_6F_5 (**1e**), were all successfully synthesized (Scheme 2) from quinuclidine, their respective silver(I) precursors, **Ag-(a–e)**, and elemental iodine in a 1:1:1 stoichiometry via silver(I) to iodine(I) cation exchange²⁸ and were characterized in the solid state by SCXRD (Figure 1). Unfortunately, the silver(I) intermediates $RC(O)O-Ag-quin$, akin to the 2-coordinate $[N-Ag-N]^+$ complexes readily isolated as intermediates in the synthesis of $[N-I-N]^+$ iodine(I) complexes,^{33,34,44,45} could not be isolated due to their reactivity in CH_2Cl_2 , poor solubility in MeCN, and apparent degradation in more polar solvents like $(CH_3)_2SO$, as had been previously observed for the similar $[I(quin)_2]^+$ complexes.⁴⁰ However, this is unsurprising, given the lack of

Scheme 2. Reaction Scheme for the Preparation of the First Hypoiodite Complexes Incorporating Tertiary Amines, Either Quinuclidine (1a–e) or DABCO (2a–e), as the Stabilizing Lewis Bases

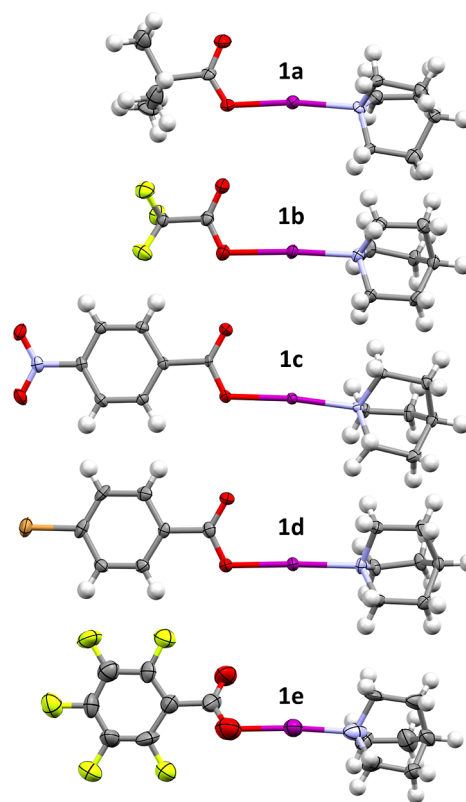
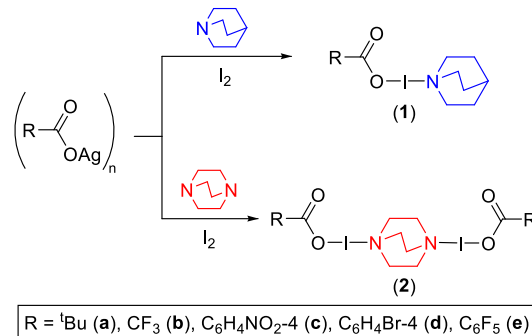


Figure 1. Solid-state structures of the carbonyl hypoiodite complexes **1a–e**, which incorporate the tertiary amine quinuclidine as the stabilizing Lewis base (thermal ellipsoids at 50% probability).

precedent for a linear $O-Ag-L$ ($L =$ tertiary amine) motif in the solid state.

The solid-state structures of the silver(I) precursors **Ag-a**, **Ag-b**, and **Ag-e** (as a hydrate) are known,^{19,46,47} so for comparison, **Ag-c** and **Ag-d** were also pursued. Unfortunately, the limited solubility of **Ag-c** meant that only the $(CH_3)_2SO$ (DMSO) adduct was obtained, **Ag-c-DMSO**, which existed as dimeric subunits of **Ag-c**, that packed into 1D-chains via the oxygen atoms of the DMSO solvates, which bridged the layers of the dimeric subunits to give $Ag\cdots Ag$ separations of 3.4177(3) and 3.4775(3) Å (Figure 2). However, the solid-state structure of **Ag-d** was obtained in a nonsolvated form and demonstrated packing as 1D polymeric chains of a dimeric subunits arrayed into bilayers, with $Ag\cdots Ag$ distances of

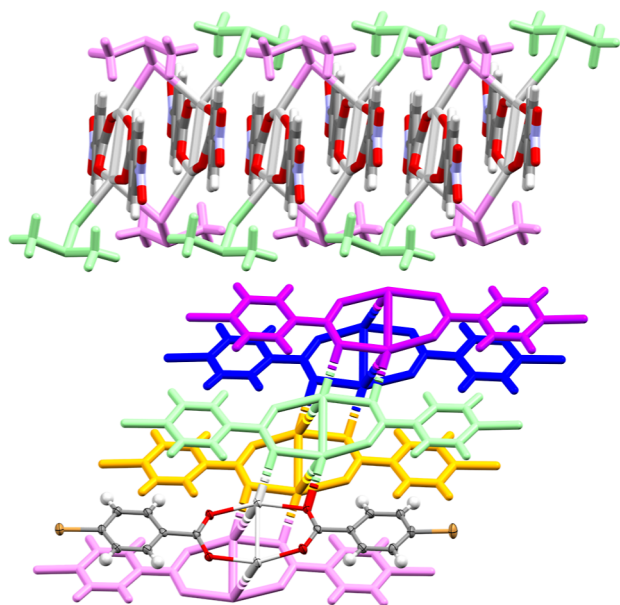


Figure 2. 1D packing of six dimeric subunits in the solid-state structures of both **Ag-c·DMSO** (top; bridging DMSO solvates block colored) and **Ag-d** (bottom; some dimeric subunits block colored for clarity; thermal ellipsoids at 50% probability), illustrating their different packing motifs as either a 1D facially coordinated chain of the dimeric subunits (**Ag-c·DMSO**) or as 1D laterally coordinated bilayers (**Ag-d**).

2.8310(4) Å within the dimeric subunits. This bilayer-packing facilitated extensive Ag⋯Ag [3.0568(5) Å] and Ag⋯O (2.489(2)/2.538(2) Å) interactions between and along the dimeric subunits, respectively, reminiscent of **Ag-a**¹⁹ but also contained a notably close and reciprocal Ag⋯Br interaction of 3.2384(6) Å (cf. van der Waals radii of Ag + Br = 3.57 Å) between neighboring polymeric chains.

It should be noted that a wide range of silver(I) carboxylate precursors, e.g., silver(I) acetate and silver(I) benzoate, were tested with quinuclidine, although no other successful hypoiodite complexes were observed. The initial hypothesis was that a strongly electron-withdrawing substituent on the carbonyl group would be best to counterbalance the quinuclidine (a strong Lewis base), resulting in the most stable iodine(I) complex possible. This was rationalized as optimally balancing the electronic environments of the two sides of the hypoiodite, consistent with the solid-state observations that the intramolecular distances between the two coordinating groups around the iodine atom, both in cationic [N–I–N]⁺ and neutral O–I–N iodine(I) complexes, were found to effectively constant (i.e., N⋯N and O⋯N, respectively) at ~4.45 Å.^{28,48} However, the observation of the pivalic acid derivative **1a**, for which the ^tBu group is electron-donating in nature, does undercut this observation, suggesting that other factors may also play a role in the stability of tertiary amine-stabilized hypoiodites.

A general description for the hypoiodite subclass of iodine(I) complexes as O–I–N (or O⋯I⋯N), analogous to the homoleptic [N–I–N]⁺ (or [N⋯I⋯N]⁺) Barluenga-type iodine(I) complexes, is commonly proscribed,⁴⁹ despite their heteroleptic coordination sphere. However, while the aforementioned O⋯N intramolecular distance of hypoiodite complexes is fairly constant, a large amount of work has been conducted to skew the iodine atom between the oxygen

and nitrogen coordinating atoms, especially in prior hypoiodite research, where this relative displacement of the iodine atom along this intramolecular O⋯N continuum can be tuned via rational design.^{17,19,37} The relative displacement of the iodine atom can differentiate between the two extreme descriptions as either a stabilized hypoiodite, O–I⋯L (L = Lewis base), or alternatively, having increased cationic iodine(I)-Lewis base character as O[−]⋯I⁺–L, with O–I/I–N distances ranging from 2.136(10)/2.324(10) to 2.308(4)/2.167(4) Å for carbonyl hypoiodites, respectively,^{16,17} and with the greatest displacement of the iodine (from the oxygen atom) to date being recently observed for kinetically trapped sulfonate derivatives [cf. O–I/I–N = 2.331(2)/2.140(3) Å].⁵⁰

A summary of the salient SCXRD-determined values is given in [Table 1](#). These results reveal that the complexes that

Table 1. O–I and I–N (in Å) Bond Lengths, and the O–I–N Bond Angles (in °) for Complexes **1a–e**, as Determined by SCXRD

complex	O–I (Å)	I–N (Å)	O–I–N (deg)
1a (^t Bu)	2.22(1)	2.285(9)	172.9(4)
1b ^a (CF ₃)	2.30(2)	2.207(7)	176.1(5)
	2.327(5)	2.232(4)	175.4(1)
1c (C ₆ H ₄ NO ₂ -4)	2.243(2)	2.254(2)	174.02(7)
1d ^b (C ₆ H ₄ Br-4)	2.233(5)	2.269(5)	177.6(2)
	2.224(5)	2.278(5)	177.1(2)
	2.229(5)	2.283(5)	176.2(2)
1e (C ₆ F ₅)	2.33(4)	2.21(4)	174(1)

^aThe CF₃C(O)OI moiety was found to be disordered in the solid-state structure of complex **1b**. ^bThree crystallographically independent molecules of **1d** were present in the asymmetric unit cell.

demonstrated the greatest cationic character (O⋯I–L; i.e., shortest I–N bond lengths) in the solid state were complexes **1b** (2.207(7)/2.232(4) Å) and **1e** (2.21(4) Å), which were indistinguishable from a 3σ tolerance. These complexes (to a 3σ tolerance) also demonstrated the longest O–I bond lengths of 2.30(2)/2.327(5) Å (**1b**) and 2.33(4) Å (**1e**), in agreement with the aforementioned empirical observation of effectively equal intramolecular O⋯N distances for previously reported O–I–N hypoiodite complexes (as shortened I–N bond lengths would be expected to be concomitant with O–I elongation).^{17,48} Inversely, the shortest O–I (2.22(1) Å) and longest I–N (2.285(9) Å) bond lengths were observed for **1a**, as expected for the carbonyl bearing the most electron-donating substituent (^tBu), though interestingly, these bond lengths were within a 3σ tolerance of those for **1d** (C₆H₄Br-4), possibly indicating that in the absence of a strong electronic influence, other factors dominate the halogen bonding. Overall, the range of the observed O⋯N intramolecular distances was 4.900(3) (**1c**) to 4.555(6) (**1b**) Å (**1a–e**: average = 4.509 Å).

This narrow range of intramolecular distances between the coordinating atoms of the iodine(I) center is also observed for [N–I–N]⁺ type complexes (i.e., N⋯N distances) at ~4.50 Å and has been observed to be effectively insensitive to varying of the substituents of the Lewis bases incorporated; e.g., [I(4-dimethylaminopyridine)₂]SbF₆ (no structural available for the BF₄ analogue),²² [I(pyridine)₂]BF₄,⁵¹ and [I(4-trifluoromethylpyridine)₂]BF₄ (as a [H(4-trifluoromethylpyridine)]BF₄ cocrystal)²⁴ have N⋯N intramolecular distances of 4.492(9), 4.51(1), and 4.521(7) Å, respectively. This extends to isomers as well (from the limited examples available), where the N⋯N

intramolecular distances of 3- or 4-aminopyridine (4-NH₂py) and 3- or 4-dimethylaminopyridine (DMAP) [N–I–N]⁺ complexes [I(3-NH₂py)₂]PF₆ (4.524(6) Å),²¹ [I(4-NH₂py)₂]Cl (4.493(4)–4.506(4) Å; no PF₆ analogue previously reported),⁵² [I(3-DMAP)₂]PF₆ (4.51(1) Å),²¹ and [I(4-DMAP)₂]PF₆ (4.487(6) Å; as a CH₂Cl₂ solvate)³³ all have values within 0.04 Å of each other. Even in the heteroleptic [N–I–N]⁺ complex, [I(4-DMAP)(1-methyl-1,2,3-triazole)]PF₆ has N⋯N intramolecular distances of 4.50(1) and 4.52(1) Å (as there are two crystallographically independent molecules present in the asymmetric unit cell). This narrow range of O⋯N (and N⋯N) intramolecular distances supports the idea of the iodine(I) center enforcing the global bonding parameters such as the O⋯N intramolecular distance, while the ligands incorporated dictate the local bonding parameters like the O–I/I–N bond lengths, which can be reliably tailored through intelligent ligand design.¹⁷ In contrast to cationic [N–I–N]⁺ and neutral O–I–N complexes incorporating aromatic Lewis base analogues, which can demonstrate characteristically large coordination shifts in their ¹⁵N NMR chemical shifts relative to their free ligands of >100 ppm,^{17–19,22,33,53} the limited data for tertiary amine [N–I–N]⁺ complexes indicate that this coordination is comparatively tame (N.B., there are no prior examples of O–I–L complexes where L is a tertiary amine).⁴⁰ Nevertheless, solution studies of **1a–e** were attempted, although unfortunately, the stability of the complexes in solution proved poor, even in dry solvents under an inert atmosphere. This was observed for initially clean samples decomposing over time during the acquisition of ¹H–¹⁵N HMBC experiments, ultimately yielding the ¹⁵N NMR chemical shift of free quinuclidine. This issue was perhaps exacerbated through the use of CD₃CN (rather than the more common CD₂Cl₂) due to the observed reactivity of tertiary amines with CH₂Cl₂ in the presence of silver(I) complexes,⁴⁰ with the more polar CD₃CN potentially disfavoring the neutral hypiodite complexes and encouraging decomposition.

Prior attempts to incorporate nonbicyclic tertiary amines in the synthesis of iodine(I) complexes had found that they were much more reactive than their bicyclic counterparts such as quinuclidine.⁴⁰ However, there had been prior success using the bicyclic diamine DABCO as a monotopic halogen bond acceptor to synthesize both discrete and supramolecular iodine(I) complexes via [N–I–N]⁺ halogen bonding.^{34,42} This presented an intriguing opportunity to utilize DABCO, in a manner analogous to quinuclidine in **1a–e**, via both of its tertiary amines in a ditopic manner.

Only four prior solid-state examples of DABCO acting as a ditopic halogen bond acceptor exist in the literature, two of which involve halogen bonding to the bromine atoms of two molecules of Br₂ or *N*-bromosuccinimide.^{54,55} The only iodine examples are both of a piperazine-functionalized fullerene coordinating to two molecules of ICl or I₂ with I–N bond lengths of 2.429(3)/2.459(3) Å or 2.606(4) Å, respectively, though the latter is perhaps best described as N⋯I–I coordination.⁵⁶ The use of HMTA as a ditopic halogen bond acceptor has also been explored with HMTA·(ICl)₂,⁵⁷ with I–N bond lengths of 2.328(3)/2.360(3) Å.

Given the intrinsic heterolepticity of carbonyl hypiodites, the polymeric structure expected for the homoleptic [N–I–N]⁺ motif when both nitrogen donor atoms are acting as ligands (i.e., a [DABCO–I⁺–DABCO–I⁺–DABCO–I⁺–] polymer) can be circumvented, allowing discrete *bis*-iodine(I) complexes to be synthesized. Such complexes would be the

inverse of previously reported *bis*- and *tris*(O–I–N) hypiodite complexes,^{16,18,19} which comprised an organic spine incorporating two or more carbonyl functional groups that could accommodate multiple I–L groups. Instead, a DABCO core would support two RC(O)O–I groups via both of its tertiary amines acting as Lewis bases, which would be attractive for their potential as double-iodination reagents if they could be isolated as pure complexes.

Analogous syntheses as complexes **1a–e** were attempted for DABCO with the same silver(I) precursors, Ag-(a–e), and elemental iodine, but this time in a 1:2:2 stoichiometry, which resulted in the observation of the *bis*(O–I–N) hypiodite complexes **2a**, **2b**, and **2e** by SCXRD (Scheme 2; Figure 3). As with **1a–e**, solution studies were attempted in CD₃CN for **2a–e**, though these complexes suffered from the same issues as previously described for **1a–e**.

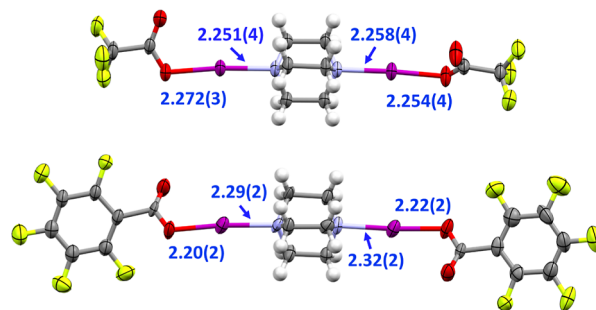


Figure 3. Solid-state structures of the *bis*(O–I–N) carbonyl hypiodite complexes **2b** (top) and **2e** (bottom), which incorporate the tertiary amine DABCO in a ditopic manner as the stabilizing Lewis base, annotated with the O–I and I–N bond lengths in Å (thermal ellipsoids at 50% probability).

The solid-state structures of **2a**, **2b**, and **2e** varied in the quality of their SCXRD models, which reflected their stability and the necessity of growing them at low temperatures (253 K). The crystals of **2a** especially were prone to degradation at room temperature and even during data collection with Cu radiation at 120 K. As a consequence, the resulting model of **2a** was of a quality where only the heavy atoms ($Z = >Si$) could be modeled anisotropically; therefore, it should only be used to confirm the identity and connectivity of the complex, and the bonding parameters will not be discussed due to their low accuracy. Nevertheless, the structures of **2b** and **2e** were of the usual high quality expected from SCXRD.

Both **2b** and **2e** contained a single molecule in their asymmetric unit cells, giving rise to pairs of O–I and I–N bond lengths, which were nevertheless indistinguishable to a 3σ tolerance in both solid-state structures. The O–I–N bond angles were as expected (**2b** = 174.8(2)/173.0(2)^o; **2e** = 174.7(8)/175.8(8)^o), in accordance with other hypiodite complexes incorporating aromatic Lewis bases, with only minor deviations from linearity. However, the O–I bond lengths of **2b** (2.254(4)/2.272(3) Å) and **2e** (2.20(2)/2.22(2) Å) were, surprisingly, quite different from their respective quinuclidine analogues **1b** (cf. 2.30(2)/2.327(5) Å) and **1e** (cf. 2.33(4) Å). The I–N bond lengths of **2b** (2.258(4)/2.251(4) Å) and **2e** (2.29(2)/2.33(2) Å) showed the same disparity when compared to those of **1b** (cf. 2.207(7)/2.232(4) Å) and **1e** (cf. 2.21(4) Å), which may suggest that the N-donor atoms of the DABCO, when utilized in a ditopic manner, are more interdependent than would be expected for

two alkyl-tethered tertiary amines. These observations would be expected for aromatic ligands like pyrazine, where the coordination of one of the nitrogen atoms is known to quench the basicity of the second nitrogen atom, though are unexpected for nonaromatic ditopic ligands like DABCO. These observations are significant given that when comparing quinuclidine and DABCO as monotopic ligands, via examination of the I–N bond lengths of the iodine(I) complexes $[\text{I}(\text{quin})_2]\text{PF}_6$ (2.301(3) Å; I–N bonds equivalent by symmetry) and $[\text{I}(\text{DABCO})_2]\text{PF}_6$ (two independent molecules present in the asymmetric unit cell: 2.292(4)/2.295(4), 2.297(4)/2.305(4) Å,^{34,40} they are comfortably within a 3σ tolerance for all values. These observations indicate that complexes **2b** and **2e** are potentially more than the sum of their parts and perhaps should not be viewed simply as fused-pairs of their respective quinuclidine analogues **1b** and **1e**. The same anti-cooperative effect was also observed in the solid-state structures of $(\text{quin})(\text{I}_2)$ and $(\text{DABCO})(\text{I}_2)_2$,^{40,58} where the I–N bond lengths of $(\text{quin})(\text{I}_2)$ are 2.35(1) and 2.368(7) Å (from two different crystallographic polymorphs), while in $(\text{DABCO})(\text{I}_2)_2$, they are between 2.41(2) and 2.43(2) Å (multiple crystallographically independent molecules present in the asymmetric unit cell). Unfortunately, given the limited examples available, a more thorough investigation is perhaps premature. Nevertheless, this observed anti-cooperative effect for an alkyl-tethered ditopic ligand is intriguing and warrants future investigation if more examples can be obtained.

High-level DFT computational studies were performed on all 10 complexes (Table S1), including on those that could not be conclusively identified by SCXRD (**2c** and **2d**), and compared to the prior experimentally determined SCXRD structures of **2b** and **2e** (Figure 4). The geometry

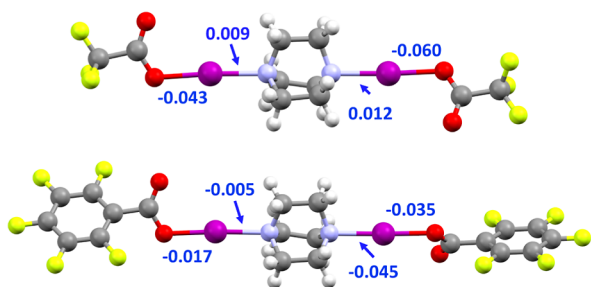


Figure 4. DFT structures of the *bis*(O–I–N) carbonyl hypiodite complexes **2b** (top) and **2e** (bottom), annotated with the differences in their O–I and I–N bond lengths from the SCXRD structures (in Å; positive values indicate that the bond lengths were overestimated in the calculated structures, and vice versa, negative values indicate that the bond lengths were underestimated).

optimizations were done at the M06-2X/def2-TZVP level of theory⁵⁹ in the SPARTAN20 program⁶⁰ with acetonitrile (dielectric = 37.50) as the solvent and using a conductor-like polarizable continuum model (C-PCM).^{61,62} This level of theory has proved to excellently reproduce the molecular geometries obtained from the SCXRD studies of $[\text{N}–\text{I}–\text{N}]^+$ and R–C(O)O–I–N (hypiodite) halogen-bonded iodine(I) complexes.^{6,17–19,26,27,33,38,40,45,50,57}

The DFT structures generally showed excellent agreement with the experimentally determined structures, with most values falling within a ± 0.01 – 0.03 Å range and a maximum discrepancy of 0.086 Å for the O–I bond length of **1e**, though this discrepancy might have been exacerbated by the twinned

data refinement of the solid-state structure of **1e** (see Supporting Information). The calculated structures for **2c** and **2d** (**2c**_DFT and **2d**_DFT, respectively), for which the SCXRD structures were not observed, indicated the same divergence from their quinuclidine analogues **1c**_DFT and **1d**_DFT, with noticeably shorter O–I and longer I–N bond lengths for the ditopic DABCO complexes, which in both cases predicted differences of ~ 0.05 Å (for **1c**_DFT vs **2c**_DFT and **1d**_DFT vs **2d**_DFT). It should be noted that the experimentally determined structures of **1c** and **1d** matched the calculated models well, with maximum differences of 0.03 Å (O–I) and <0.01 Å (I–N) for **1c** and 0.03 Å (O–I) and 0.02 Å (I–N) for **1d**.

CONCLUSIONS

In conclusion, the first examples of carbonyl hypiodites incorporating tertiary amines as the stabilizing Lewis base have been synthesized by using the bicyclic tertiary amines quinuclidine (**quin**; **1a–e**) and DABCO (**2a**, **2b**, and **2e**). A variety of silver(I) carboxylate precursors (RC(O)OAg) were screened, though those bearing electron-withdrawing substituents (e.g., CF_3 and C_6F_5) ultimately proved successful, with the only exception being $^t\text{BuC}(\text{O})\text{OAg}$ (**Ag-a**), which was also identified for both quinuclidine and DABCO. These tertiary amine hypiodites were observed to be more reactive than analogues incorporating aromatic N-donor ligands (e.g., pyridine derivatives), which prevented reliable solution studies such as the ^1H – ^{15}N HMBC experiment being used to determine the ^{15}N NMR coordination shift. However, these tertiary amine hypiodites were conclusively isolated in the solid state by SCXRD. The solid-state results revealed that these tertiary amine hypiodites also maintained a generally constant intramolecular O \cdots N distance of ~ 4.52 Å, which was slightly larger than that observed for their aromatic analogues (cf. ≈ 4.45 Å). The tertiary amine hypiodites demonstrated the same adaptability as prior hypiodite complexes in their ability to induce movement of the relative position of the iodine(I) center betwixt the two donor atoms; electron-donating groups (^tBu) on the carbonyl ligand induced short O–I bond lengths (and concomitantly long I–N bond lengths), and vice versa, electron-withdrawing substituents (C_6F_5) induced long O–I bond lengths (and shorter I–N bond lengths), with differences of over 0.1 Å being observed between these two extremes (i.e., a greater difference in bond lengths than the entire range of distances observed for $[\text{N}–\text{I}–\text{N}]^+$ iodine(I) complexes incorporating a myriad of pyridine derivatives). The *bis*(O–I–N) complexes **2a–e**, though not the first examples of such a motif as *bis*- and *tris*(O–I–N) complexes based on di- and tricarboxylic acid skeletons are known, are the first examples of the motif based on a ditopic Lewis base skeleton. The ditopic DABCO complexes demonstrated interesting deviations in their solid-state bond lengths compared to the monotopic quinuclidine complexes (**1a–e**), suggesting an unexpected interdependence in the two tertiary amine groups of the DABCO. These deviations were also not observed in iodine(I) complexes incorporating DABCO as a monotopic ligand, which offers tantalizing unforeseen potential for future *multi*-hypiodite complexes.

EXPERIMENTAL SECTION

General Considerations. All reagents and solvents were obtained from commercial suppliers and used without further purification. The synthesis of the silver(I) precursors (**Ag-a**, **Ag-c**, and **Ag-e**) was

performed as previously described.^{17,19} For structural NMR assignments, ¹H NMR and ¹H–¹⁵N NMR correlation spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer at 298 K in CD₃CN or (CD₃)₂SO. Chemical shifts are reported on the δ scale in ppm using the residual solvent signal as internal standard (cf. (CH₃)₂SO in (CD₃)₂SO: δ_H 2.50). For the ¹H NMR spectroscopy, each resonance was assigned according to the following conventions: chemical shift (δ) measured in ppm, observed multiplicity, observed coupling constant (*J* Hz), and number of hydrogens. Multiplicities are denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad).

The single-crystal X-ray data were collected at 120 K using mirror-monochromated Cu Kα (λ = 1.54184 Å) radiation either on an Agilent SuperNova dual wavelength diffractometer fitted with an Atlas (1a–1d) or HyPix-Arc 100 (Ag-b, 2a, and 2b) detector or on a Rigaku XtaLAB Synergy-R diffractometer with a HyPix-Arc 100 detector (Ag-c-DMSO, Ag-d, 1e, and 2e). All structures were solved by intrinsic phasing (SHELXT)⁶³ and refined by full-matrix least-squares on *F*² using Olex2,⁶⁴ utilizing the SHELXL module.⁶⁵ Anisotropic displacement parameters were assigned to non-H atoms, and isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with U_{iso}(H) = 1.2 U_{eq}(CH, NH₂) or U_{iso}(H) = 1.5 U_{eq}(CH₃, H₂O) of their respective parent atoms. The X-ray single-crystal data and CCDC numbers (2337455–2337465) of all new structures are included below.

Please refer to the Supporting Information for details of the synthesis, characterization, and DFT calculations of all the complexes described herein.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.cgd.4c00377>.

Synthesis and characterization, NMR spectra, SCXRD comparison, and computational details (PDF)

Accession Codes

CCDC 2337455–2337465 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Kari Rissanen – Department of Chemistry, University of Jyväskylä, Jyväskylä 40014, Finland; orcid.org/0000-0002-7282-8419; Email: kari.t.rissanen@jyu.fi

Jas S. Ward – Department of Chemistry, University of Jyväskylä, Jyväskylä 40014, Finland; orcid.org/0000-0001-9089-9643; Email: james.s.ward@jyu.fi

Author

Shilin Yu – Department of Chemistry, University of Jyväskylä, Jyväskylä 40014, Finland

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.cgd.4c00377>

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Notes

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■ ABBREVIATIONS

DABCO, 1,4-diazabicyclo[2.2.2]octane; DMSO, dimethyl sulfoxide (Me₂SO); quin, quinuclidine (1-azabicyclo[2.2.2]-octane)

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