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Complexes of *N*-chloroquinuclidinium with chloride: strong halogen bonding *via* chlorine atoms†

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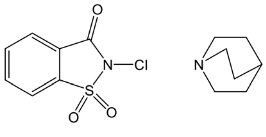
Crystallization of *N*-chlorosaccharin with quinuclidine (QN) produced QN-Cl$^+$ cations showing a covalent bond between chlorine and a tertiary nitrogen atom. Strong (supramolecular) halogen bonds between the QN-Cl$^+$ and Cl$^-$ anions in their 2 : 1 and 1 : 1 complexes comprise a large contribution of orbital (covalent) interactions.

Halogen bonding (HaB) has emerged in recent years as one of the most powerful tools in molecular recognition, crystal engineering, and catalysis.[1] Yet, while fluorinated and chlorinated molecules are prevalent in chemical and biological systems, studies of halogen bonding have predominantly focused on iodine- and bromine-containing HaB donors. This choice is due to the stronger attraction of the electron-rich species to electrophilic bromine and iodine (due to their higher polarizability, and thus higher positive electrostatic potentials on their surfaces) which facilitates applications of these interactions.[1] Publications describing HaB with chlorine atoms are relatively rare, and the existence of halogen bonding *via* fluorine is a subject of debate.[1–5] Furthermore, bromine and iodine-containing HaB donors form associations with the HaB lengths spanning a wide range of distances from van der Waals separations to nearly covalent bonds.[6,7] In contrast, there are only a few examples of strong halogen bonds involving chlorine, where bond lengths are at least 15% shorter than the van der Waals separations,[8,9] and an in-depth analysis of these interactions is lacking.

To evaluate strong HaB *via* chlorine, we turned to the interaction of *N*-chlorosaccharin, ClSac, with quinuclidine, QN, (Scheme 1). Indeed, *N*-iodo- and *N*-bromosubstituted imides are strong HaB donors that form short halogen bonds (approaching covalent bond lengths) with various nucleophiles.[10,11] Yet, the structural characterization of similar complexes with *N*-chlorosubstituted imides was hindered by their rapid decomposition.[11] Only a structure of a 2:1 complex of succinimide (ClSim) with a Cl$^-$ anion (showing N–Cl⋯Cl$^-$⋯Cl–N bonds with Cl⋯Cl distances of 2.892 Å and 2.898 Å) has been reported,[9] and even the structure of ClSac itself was not available in the crystallographic databases. On the other hand, QN is a very strong HaB acceptor, and its interaction (or that of its analog, 4-diazabicyclo[2.2.2]octane, DABCO) with strong HaB donors produced HaB complexes or iodonium and bromonium cations.[7,12,13]

Evaporation of solutions of ClSac in dichloromethane or acetonitrile produced monoclinic (colourless) crystals **1**.‡ They show short contacts between chlorines and (carbonyl) oxygens of neighbouring ClSac molecules (Fig. S1 in the ESI†). The two non-equivalent Cl⋯O(C) contacts are 10% and 15% less than the sum of the van der Waals radii (Fig. S1,† Table 1). Accordingly, one of them is markedly shorter than those observed in the reported crystals of ClSim (2.841 Å) and *N*-chlorophthalimide (2.946 Å).[9,14] Besides, crystals **1** also show short C–H⋯O contacts with sulphur-bound oxygens.

Slow evaporation of the solutions containing ClSac and QN in propionitrile resulted in halogen transfer and formation of crystals **2** and **3** of *N*-chloroquinuclidinium cations (ClQN$^+$) with saccharinate (Sac$^-$) and/or Cl$^-$ anions.§



ClSac QN

Scheme 1 Structures and acronyms of the molecules.

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Table 1 Geometric characteristics of N–Cl (intramolecular) and Cl⋯X (intermolecular) bonds in crystals **1–3**

Crystal	$d_{\text{N–Cl}}$, Å	$d_{\text{Cl}\cdots\text{X}}$,[a] Å	∢N–Cl⋯X, deg
1[b]	1.6762(10)	2.9499(9)	168.80(4)
	1.6906(9)	2.7538(9)	176.65(4)
2	1.804(4)	2.6643(12)	176.15(14)
3[b]	1.7861(18)	2.7917(8)	177.56(6)
	1.7807(19)	2.9193(8)	177.01(7)

[a] X=O in **1**, and X=Cl in **2** and **3**. [b] Two sets of bonds (see the text).

Analogous cations were suggested as the critical intermediates of the DABCO-catalyzed chlorinations of various substrates using *N*-chloroimides (which is a much more convenient and greener source of chlorine than Cl_2).[15] However, their structures were not established. In fact, **2** and **3** represent the first X-ray structures showing a N–Cl bond between chlorine and a tertiary nitrogen atom.¶ They also show very short N–Cl⋯Cl^- halogen bonds (Table 1). In particular, colourless orthorhombic crystals **2** (space group *Cmc*2_1) comprise layers of $ClQN^+$ cations and Cl^- anions (Fig. S2 in the ESI†). Besides the N–Cl⋯Cl^- halogen bonds, each chloride forms six H-bond-(HyB) like C–H⋯Cl short contacts with the surrounding QN moieties (Fig. 1). The covalent N–Cl bond length of 1.804(4) Å is similar to the longest N–Cl bonds found in the Cambridge Crystallographic Database (bonds with three-membered aziridine, 1.791 Å, or oxaziridine, 1.796 Å, rings).[17] The (intermolecular) Cl⋯Cl distance of 2.664 Å in **2** (Table 1) is 24% shorter than the sum of the van der Waals radii of the chlorine atoms.

Evaporation of the solution of ClSac and QN also produced pale yellow orthorhombic crystals **3** in space group *Pbca*. They comprise pairs of $ClQN^+$ cations linked by Cl^- anions (Fig. 2 and S3 in the ESI).† The positive charges of such triads are balanced by the Sac^- anions. The N–Cl⋯Cl^-⋯Cl–N fragment in **3** (sometimes labeled bifurcated or three-centered bonds[18]) is characterized by the larger intermolecular N–Cl⋯Cl distances and the shorter intramolecular N–Cl bonds as compared to the corresponding values in **2** (Table 1, note that the overall number of the contacts between Cl^- and $ClQN^+$ in **3** were the same as in **2**, but five contacts in **3** are related to HyB).

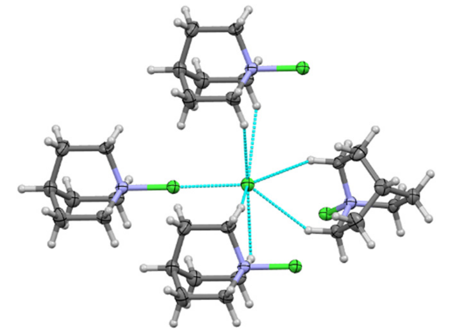

Fig. 1 X-ray structure of **2** showing short contacts (light blue lines) of $ClQN^+$ cations with Cl^- anions.

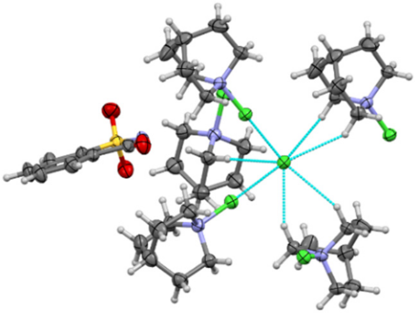

Fig. 2 Structure of **3** (blue lines show short contacts between Cl^- and QN-Cl^+).

Quantum mechanical computations of the $ClQN^+{\cdot}Cl^-$ and $(ClQN^+)_2{\cdot}Cl^-$ complexes produced optimized structures similar to that in the solid state (Fig. S4 in the ESI†). The intramolecular N–Cl bonds in the optimized structures (1.801 Å and 1.769 Å in $ClQN^+{\cdot}Cl^-$ and $(ClQN^+)_2{\cdot}Cl^-$, respectively) were within 0.02 Å of the experimental values in Table 1. The Cl⋯Cl^- distances in the optimized structures were very short (2.641 Å, 2.793 Å in $ClQN^+{\cdot}Cl^-$ and $(ClQN^+)_2{\cdot}Cl^-$, respectively). This supported the idea that the short N–Cl⋯Cl^- distances in **2** and **3** resulted mainly from the HaB *via* chlorine atom, and not from other crystal packing forces. Furthermore, the HaB length in **3** is in the same range as the analogous N–Cl⋯Cl^- distances in the 2 : 1 HaB complexes of ClSim (*vide supra*). However, while in the $(ClSim)_2{\cdot}Cl^-$ complexes, Cl^- is attracted to the neutral molecule, the bonding in **2** and **3** occurs between cationic HaB donors and anionic HaB acceptors. This allows us to compare the bonding characteristics of the differently charged HaB donors which involve similar atoms and have comparable HaB lengths.

The molecular electrostatic potentials of ClSac and $ClQN^+$ are shown in Fig. 3. The ClSac molecule has a distinct area of positive potential along the N–Cl bond (σ-hole). The surfaces of hydrogen substituents in this molecule are also positive, which is consistent with the presence of short contacts of (negatively charged) oxygens with both chlorine and hydrogens in the X-ray structure of ClSac. As expected for the cationic species, the potential of $ClQN^+$ is positive over all its surface. Similar to ClSac, it shows a σ-hole along the extension of the N–Cl bond. The potentials at the terminus of

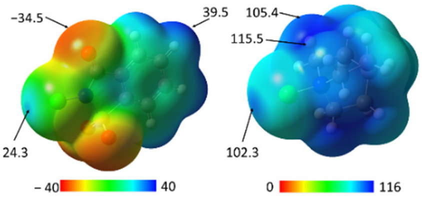

Fig. 3 Surface electrostatic potentials (in kcal mol^{-1}, at 0.001 a.u. electron density) of ClSac and $ClQN^+$ (see ClSim in Fig. S6 in the ESI†).

the hydrogen atoms near the nitrogen side of $ClQN^+$ are about the same as that at the σ-hole of chlorine (the most positive potentials on the surfaces of these cations are found in the valley between these hydrogens). This is also consistent with the patterns of HaB and HyB in the crystals of $ClQN^+$ with Cl^- anions. Nonetheless, the current work is focused on the characteristics of the most unusual of these interactions, *i.e.*, the N–Cl···Cl^- halogen bonds *via* chlorine atoms.

QTAIM analysis[19,20] of the fragments of crystals **1–3** together with the complex of Cl^- with ClSim revealed bond paths and (3, −1) bond critical points (BCPs) between chlorine substituents and Cl^- anions or oxygen substituents (Fig. 4 and S5 in the ESI†). Characteristics of these BCPs are listed in Table 2 (see Table S2 in the ESI† for details) together with the characteristics of the adjacent N–Cl (intramolecular) bonds.

Although one of the Cl···O bonds in **1** is 0.2 Å shorter than the other, the electron and energy densities at BCPs located on their bond paths (Table S2 in the ESI†) are close, and their average values (Table 2) are consistent with typical intermolecular bonds.[20] Specifically, small positive values of the energy density at the BCPs for Cl···O bonds are common for the electrostatically driven intermolecular interactions. The electron densities of 0.01 a.u. at these points are more than an order of magnitude lower than that of the adjacent intramolecular N–Cl bond. The Mayer bond order[21] of the Cl···O bond is negligible. In comparison, the BCP of the Cl···Cl^- bond in **2** is characterized by $\rho(r)$ = 0.04 a.u. and small and negative energy density. This suggests a contribution of a covalent component to this bonding. Such suggestion is supported by the large (as for supramolecular bonding) ELF and MBO values found for this bond (Table 2). The characteristics of the Cl···Cl^- bonds in **3** and in the 2 : 1 complexes of ClSim with Cl^- are intermediate between that of the Cl–O and Cl–Cl bonds in **1** and **2** (in agreement with differences in the interatomic distances in these complexes). The characteristics of the C–H···Cl^- contacts in crystals **2** and **3** (*e.g.*, $\rho(r) \sim 0.01$ a.u., small positive $H(r)$ values, negligible MBOs, see Table S2 in the ESI†) are consistent with the moderately strong, electrostatic interactions.

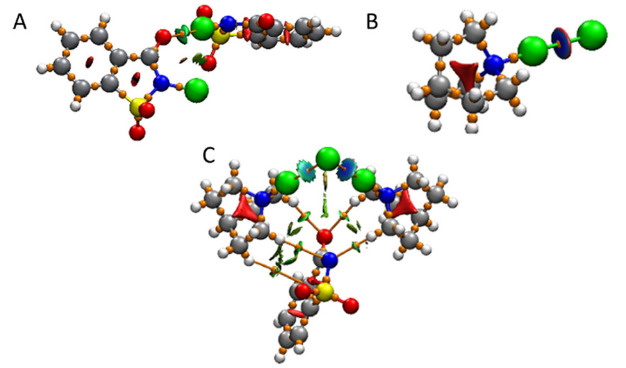

Fig. 4 QTAIM and NCI analyses of the structures of HaB complexes in **1** (A), **2** (B), and **3** (C). The bond paths and critical (3, −1) points (QTAIM) are shown as orange lines and spheres, and blue-green areas (NCI) indicate bonding interactions.

NCI analysis[22] confirmed the trend revealed by the QTAIM and MBO analyses. Specifically, the HaB dimer in **1** showed a small green area around the BCP on the C···O bond path (Fig. 4A). This indicates a weak non-covalent attraction between these atoms. In comparison, the HaB complex in **2** showed a dark blue area around BCP on the Cl···Cl^- bond path, which is consistent with the strong supramolecular bonding. The light-blue areas around the BCP on the Cl···Cl^- bond path in **3** and in the 2 : 1 complex formed by ClSim and Cl^- (Fig. S5 in the ESI†) are intermediate between those in **1** and **2**. The QTAIM characteristics of the bonding in 2 : 1 complexes in **3** and $(ClSim)_2Cl$ are also close (Table 2). This indicates that while the potential at the σ-hole of the $ClQN^+$ cation of 102 kcal mol^{-1} is much higher than that of 21 kcal mol^{-1} on the surface of ClSim, the topologies of the electron and energy densities in these complexes are close. To evaluate the distinctions in bonding with these cationic and neutral HaB donors, we carried out an energy decomposition analysis (EDA).

The AMS suite of programs decomposes the intermolecular interaction energy, ΔE_{int}, into electrostatic, ΔE_{es}, Pauli repulsion, ΔE_{Pauli}, orbital (charge-transfer) interaction, ΔE_{oi} and dispersion, ΔE_{disp}, components.[23] An analysis of the 1 : 1 and 2 : 1 complexes in **2**, **3** and $(ClSim)_2{\cdot}Cl^-$ (using coordinates extracted from the crystal structures) showed that the attraction between Cl^- anions and HaB donors is determined by a combination of ΔE_{es} and ΔE_{oi}, and less than 5% contribution of dispersion (Table S3 in the ESI†). The ΔE_{es} in the complexes of $QNCl^+$ with Cl^- were about twice as large as ΔE_{oi}. Yet the latter contributed substantially (34% and 27% in 1 : 1 and 2 : 1 complexes, respectively) to the intermolecular (charge-assisted) halogen bonding. The contribution of ΔE_{oi} of 59% in $(ClSim)_2{\cdot}Cl^-$ complexes is larger than that of ΔE_{es} (36%). The contributions of ΔE_{disp} and ΔE_{oi} to the bonding in $(ClSac)_2$ are both about 25%, and the magnitude of ΔE_{es} is about twice as high.

Overall, the structure of ClSac (**1**) showed short N–Cl···O=C distances indicating strong halogen bonding *via* chlorine atoms. Yet, the crystallization of ClSac with QN produced the $ClQN^+$ cations (instead of the HaB complexes between ClSac and QN). While similar cations were suggested as the intermediates in the DABCO-catalyzed chlorination of various substances by *N*-chloroimides,[15] this work presents the first X-ray structure of such species. Notably, $ClQN^+$ comprises a covalent bond between chlorine and a tertiary nitrogen atom. Although bonds between such atoms and fluorine have been reported,[24] crystals **2** and **3** show the first structure of a similar bond with chlorine. It is worth noting that bonding between tertiary nitrogen and iodine or bromine has only been observed in iodine(I) and bromine(I) complexes with QN or DABCO (the nature of

Table 2 Electron, $\rho(r)$, and energy, $H(r)$, densities, Laplacians of electron density, $\nabla^2\rho(r)$ at BCPs, electron localization functions, ELF, and Mayer bond orders, MBO, of N–Cl and Cl⋯X bonds

Crystals	Bond	$\rho(r)$, a.u.	$H(r)$, a.u.	$\nabla^2\rho(r)$, a.u.	ELF	MBO
1[a]	N–Cl	0.23	−0.179	−0.25	0.81	0.99
	Cl⋯O	0.01	0.002	0.06	0.02	<0.05
2	N–Cl	0.18	−0.106	−0.07	0.78	1.00
	$Cl\cdots Cl^-$	0.04	−0.002	0.10	0.17	0.19
3[a]	N–Cl	0.19	−0.117	−0.11	0.81	1.05
	$Cl\cdots Cl^-$	0.03	0.001	0.09	0.11	0.12
$(ClSim)_2Cl$[b]	N–Cl	0.20	−0.138	−0.16	0.80	0.95
	$Cl\cdots Cl^-$	0.02	0.002	0.07	0.08	0.11

[a] Average characteristics of the bonds (calculated using coordinates from the solid-state structures, see Table S2 in the ESI† for details). [b] CCDC refcode WEZVUS.[9]

such bonding remains a subject of debate).[12,13] Also, $(pyridine)_2Cl^+$ and $(pyridine)Cl^+$ complexes were recently reported.[25]

Remarkably, the chlorine substituents in $ClQN^+$ form strong halogen bonds with Cl^- anions. Even if an attraction between cations and anions is expected, characteristics of the $N–Cl\cdots Cl^-$ bondings reported herein are rather unique. Firstly, this bond in **2** is very short (24% less than the van der Waals separation). In comparison, the $C–Cl\cdots Cl^-$ bond length between the similar $QN\text{-}CH_2Cl^+$ cations and Cl^- anions of 3.361 Å is just 4% shorter than the van der Waals separations.[26] Secondly, about 30% of the attractive energy in the $N–Cl\cdots Cl^-$ bonding between cations and anions is related to orbital interactions, confirming the significant role of covalency in strong halogen bonding.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre under 2384417–2384419.

Author contributions

M. H. and M. Z. – investigation, writing – review and editing, S. V. R. – conceptualization, investigation, data curation, visualization, writing – original draft, review and editing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Crystal data. **1.** $C_7H_4ClNO_3S$, M = 217.62, monoclinic, $P2_1/c$, a = 8.4794(5), b = 28.3380(18), c = 7.7102(5), β = 116.892(2)°, U = 1652.33(18) $Å^3$, T = 150 K, Z = 8, 49 424 reflections measured, 6276 unique (R^{int} = 0.026), which were used in all calculations. The final $wR(F^2)$ was 0.078 (all data). **2.** $C_7H_{13}ClN{\cdot}Cl$, M = 182.08, orthorhombic, $Cmc2_1$, a = 7.0792(8), b = 10.8984(12), c = 11.0370(13), U = 851.53(17) $Å^3$, T = 150 K, Z = 4, 3151 reflections measured, 880 unique (R^{int} = 0.045), which were used in all calculations. The final $wR(F^2)$ was 0.080 (all data). **3.** $C_7H_4NO_3S{\cdot}2(C_7H_{13}ClN){\cdot}Cl$, M = 510.89, orthorhombic, $Pbca$, a = 11.2805(14), b = 10.9819(18), c = 38.981(4), U = 4829.0(11) $Å^3$, T = 150 K, Z = 8, 61 595 reflections measured, 5252 unique (R^{int} = 0.075), which were used in all calculations. The final $wR(F^2)$ was 0.130 (all data).

§ The only source of the Cl^- in the solutions was ClSac. The surprising reproducible formation of Cl^- is probably related to the high reduction potentials of cationic and neutral forms of chlorine, (although the mechanism of this process is not clear).

¶ (a) Several earlier publications described the preparation and applications of cations in which chlorine is attached to tertiary nitrogen, *e.g.* chlorotrimethylammonium or 1,4-dichloro-1,4-diazabicyclo [2,2,2]octane,[16] but their X-ray structures are not available. (b) Note that the single crystals **2** and **3** were stable (in mother liquor) for weeks in a fridge. They were obtained as a mixture (which probably included saccharine and/or ClSac) and their isolation as pure substances and measurements of their spectral properties are planned in a separate study.

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