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Research Article

FIRST PRINCIPLES STUDY OF NaCl···A-B TYPE (A-B = ACCEPTOR) COMPLEXES

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ABSTRACT
A first-principles study of NaCl•••A-B type (A-B =acceptor) complexes was performed using ab initio methods and the Atoms in Molecules (AIM) approach. We have considered ten different acceptors: C_2H_4, NH_3, H_2O, H_2, HF, HNa, HLi, FNa, FLi, NaCl. This work reports whether these complexes form sodium bonds by examining sodium bond distances, bond angles, frequency shifts, binding energies, and topological parameters (electron density and Laplacian of electron density at sodium bond critical points). We calculated binding energies by correcting for both basis set superposition error and zero-point vibrational energies. Our findings reveal both red and blue shifts in the stretching frequency modes. The value of electron density and the value of the Laplacian of the electron density are consistent with earlier reports on sodium bonding. This study further shows that sodium bond distances are more closely related to ionic radii than to van der Waals radii, with notable differences compared to hydrogen bond radii. All these results provide the nature of sodium bonding, and its unique characteristics compared to other non-covalent interactions.

Keywords: Atoms in molecules, first principles study, sodium bonding

INTRODUCTION
Interest in the study of non-covalent interactions has been growing in recent times (Das & Arunan,2023). Several types of non-covalent interactions have already been studied. In earlier days, although both theoretical and experimental methods were conducted to explore non-covalent interactions, it was not possible to examine all types due to limitations in both approaches. However, with the implementation of quantum chemical calculations, the study of a wide range of non-covalent interactions has now become possible. These intermolecular interactions comprise hydrogen bonds, halogen bonds, lithium bonds, pnicogen bonds, chalcogen bonds, tetral or carbon bonds, etc. (Arunan et al., 2024; Adhav et al., 2023 Parajuli, 2016).

Recently, a review paper raised a question: why are there so many names for non-covalent interactions (Taylor, 2024)? Among the various non-covalent interactions, the term "hydrogen bond" was the first to be coined. The study of hydrogen bonding is generally considered to have begun with Latimer and Rodebush's seminal research on the structure and properties of water at UC Berkeley (Latimer & Rodebush, 1920). As research progressed, by taking the references of hydrogen bonding, chemists were able to identify the existence of other types of non-covalent interactions such as halogen bonding (Muller, 1994), lithium bonding (Kollman et al., 1970, Ault, 1978). Recent studies show that lithium bonding is more ionic than hydrogen/halogen bonding (Shahi & Arunan, 2014).

Since sodium is considered an analog of hydrogen and lithium, it is logically expected to substitute the hydrogen/lithium bond and potentially exhibit a similar interaction. However, the study of Na-bonding is very limited compared to the study of hydrogen bonding, halogen bonding, and lithium bonding. There are only a few theoretical reports on sodium bonding as compared to other non-covalent interactions. The publication by Kulkarni and Rao was perhaps the first to carry out a systematic study of sodium bonds, comparing their properties to those of the hydrogen and lithium bonds (Kulkarni and Rao, 1983). After a gap of many years, Zhi-Feng et al. provided a theoretical prediction regarding the characteristics of Na-bonding interactions involving various donors and acceptors (Li et al., 2009). Furthermore, Parajuli and Arunan investigated sodium-bonded Na-D···A-B complexes (D is F and OH, A-B are acceptors) using π bonds, σ bonds, and other acceptors to explain why sodium bonding is not commonly observed (Parajuli & Arunan, 2013).

To our understanding, no study has yet been performed on the nature of bonding in NaCl···A-B complexes. For this, we have used ab initio and atoms in molecules (AIM) (Foresman & Frish, 1996; Popelier et al., 2000) theoretical calculations and investigated several properties, including geometric parameters, binding energies, the Laplacian of electron density, and electron densities at Na-bond critical points, and the radius of the sodium bond. These results have then been compared with earlier reports.

MATERIALS AND METHODS
We have performed ab initio and AIM theoretical calculations to determine whether $\mathrm{NaCl\cdots AB}$ complexes form sodium bonds. The optimized geometries of $\mathrm{NaCl\cdots AB}$ complexes, have been carried out using GAUSSIAN 03 software (Frisch *et al.*, 2004).

To obtain the most stable structure of $\mathrm{NaCl \cdots A-B}$ complexes, both cyclic and linear structures were considered. All the calculations were performed in the MP2 level of theory (Møller & Plesset, 1934; Pople *et al.,* 1978) and the DFT (B3LYP) level of theory (Lee *et al.,* 1988). We used 6-311++G (d, p) basis set in this calculation to optimize the structures. To compare the results of 6-311++G (d,p) basis set we have done calculations using the aug-CC-pVDZ basis set. Like 6-311++G (d,p) basis set, this aug-CC-pVDZ basis set also includes both polarization and diffuse functions, making it suitable for studying a wide range of molecules, especially those with non-neutral charge distributions, and computationally affordable for medium-sized systems. These basis sets provide varying levels of accuracy and coverage for electron correlation and wavefunction description.

To determine whether the optimized structures are true minima, frequency calculations were conducted for all NaCl···A-B complexes. Since the Atoms in Molecules (AIM) theoretical analysis provides a deeper understanding of inter and intra-molecular interactions, we performed the AIM analysis calculating the electron density at bond critical points (ϱ) and the Laplacian of the electron density ($\nabla^2\varrho$) for $\mathrm{NaCl \cdots A-B}$ complexes. We used AIMALL software (AIMAll (Version 19.10.12), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2019) to calculate the topological parameters.

RESULTS AND DISCUSSION

In this section, we have presented the findings of this study.

Geometrical Parameters and Frequency Shifts

Geometrical parameters such as sodium bond distance ($R_{Na\cdots A}$), change in $\mathrm{Na-Cl}$ bond distance ($\Delta R_{Na\cdots cl}$), bond angle ($(\angle ClNa \cdots A)^0$), and frequency shift of $\mathrm{Na-Cl}$ stretching mode (Δv) in the MP2 level of theory using the basis sets 6-311++G (d, p) and Aug-CC-pVDZ for both linear and cyclic structures were studied. All these data are shown in Table 1. Similar types of data were found for the B3LYP level of theory. These data were presented in supplementary results (Supplementary Table S1). As the shifting of the D-H (D is the donor atom) stretching vibration is observed in non-covalent interactions such as hydrogen bonding (Raghavendra et al., 2006), we examined the frequency shift of the Cl-Na stretching vibration at both the MP2 level of theory (Table 1) and the B3LYP level of theory (Supplementary Table S1). Some structures exhibit saddle points with one or more imaginary frequencies, which are listed in Table 1. This observation suggests that certain linear structures are not favorable, like in the earlier report (Parajuli and Arunan, 2013).

Geometry and Frequency Shifts for Linear Dimers

The distance between the donor atom and the acceptor atom is measured to determine whether a non-covalent bond exists. If the bond is present, this distance must be smaller than the sum of the van der Waals radii of the donor and acceptor atoms. To find out whether there is a bonding between the Na atom and the acceptor atom (A), $Na \cdots A$ distance ($R_{Na\cdots A}$) for $lNa \cdots A-B$, the complex was measured. This distance was found to range from $2.078A^o$ to $2.899A^o$ and in almost all cases it was found to be smaller than the van der Waals radii of the Na atom and 'A' atom, indicating $Na-Cl \cdots A-B$ bonding. When examining Table 1, it is observed that Na…A distance for C_2H_4 acceptor is longest and the same with FLi acceptor is shortest. This can be explained by the nature of interactions between the donors and acceptors. For all levels of calculations, due to weak van der Waals interactions with nonpolar molecules like C_2H_4, and H_2, resulting in the largest bond distances ($R_{Na\cdots A}$) among all linear complexes that were studied, whereas with polar molecules like NH_3 and H_2O, Ion-dipole interactions lead to shorter distances. Similarly, partial ionic interactions, like those in HLi and HNa, further reduce the distance, while strong ionic interactions, such as with FLi and FNa, result in the shortest bond distances.

If bonding occurs, a change in the Na-Cl bond distance is expected. Therefore, we measured the change in $\mathrm{Na-Cl}$ distance($\Delta R_{Na\cdots Cl}$), which varies within the range $0.002A^o$ to $0.482A^o$. This positive value of $(\Delta R_{Na\cdots Cl}(A^o))$ indicates the elongation of $\mathrm{Na-Cl}$ bond during bond formation. Similarly, the bond angle between the donor molecule (NaCl, in our case) and the acceptor atom is another fingerprint for determining bonding. Hence, we measured the angle $(\angle ClNa \ldots A)^o$ for all linear complexes. In hydrogen bonding $(\angle D-H \ldots A)^o$ (D is the donor atom) this value should be more than 110^o (Arunan et al., 2011). Our study found that these values range from 174.80^0 to 180.00^0.

Another criterion for determining bonding is the change in the stretching frequency of the donor molecule. Since there is a change in the bond length of the donor molecule, a corresponding change in the stretching frequency is expected. The frequency shift of $\mathrm{Na-Cl}$ stretching mode (Δv) was measured and found to be in the range $-162.03\ \mathrm{cm^{-1}}$ to $33.39\ \mathrm{cm^{-1}}$. This indicates that the frequency shift of $\mathrm{Na-Cl}$ stretching mode exhibits both red and blue shifts.

Geometry and Frequency Shifts for Cyclic Dimers

We have measured similar geometrical parameters and frequency shifts in the case of cyclic dimers as observed in the linear dimers. The $Na \cdots Cl$ distance ($R_{Na\cdots A}$) was found to range from $2.101A^o$ to $2.559A^o$. For the cyclic dimer, the change in $\mathrm{Na-Cl}$ distance ($\Delta R_{Na\cdots cl}$) was determined, which varies between the range $0.154A^o$ to $0.203A^o$. This positive value of ($\Delta R_{Na\cdots Cl}$) indicates the elongation of $\mathrm{Na-Cl}$ bond during the bond formation. The bond angle $(\angle ClNa \cdots A)^0$ for the cyclic complexes ranges from 79.720 to 93.17^0. The variation of Na–Cl bond distance ($\Delta R_{\mathrm{Na-Cl}}$) in the cyclic dimer is slightly larger compared to that of the linear dimer. For instance, in the NaCl dimer, the value of

ΔR_{Na-Cl} for the linear structure is 0.020Å, whereas, for the cyclic configuration, it is 0.157Å at the MP2/6-311++G (d, p) level. This indicates that the change in the bond angle (∠ClNa···A) doesn't have a significant impact on the change in Na–Cl bond distance. The largest change in the bond distance observed in the cyclic dimers may be due to the fact that the nature of interactions in cyclic dimers is different from that in linear dimers. Like in the case of linear dimers, we calculated the frequency of stretching mode of donor molecule before and after complex formation and thus the change in frequency is calculated. Our calculations indicate that sodium bonding exhibits both red and blue shifting frequencies. Stationary points with one or more imaginary frequencies are observed for some structures, suggesting that some cyclic structures are either not fully optimized or not favorable for this complex formation.

Binding Energies

In an atom, the binding energy is the minimum energy that would be required to disrupt the nucleus of an atom into its constituent parts. The stability against the disintegration of any nucleus depends upon its magnitude of binding energy (McNaught & Wilkinson, 1997). Similarly, the binding energy in case of molecular complexes/ molecular clusters is defined as the energy difference between the complex and monomers. Furthermore, for an accurate value of binding energy Zero Point Vibrational Energy (ZPVE) must be taken into account, which is defined as the energy difference between the vibrational ground state and the lowest point on the Born-Oppenheimer potential energy surface (Truhlar *et al.,* 1987). It can be determined by calculating the difference between the ZPVE of the complex and the ZPVE of the monomers, i.e.,
ZPVE = ZPVE of the complex - ZPVE of the monomers.

In the present work, we have estimated the binding energy, the ZPVE, and the corrected binding energy of the complexes using MP2 level of theory with the basis sets $6-311++G(d,p)$ and Aug-CC-pVDZ basis sets. These values are summarized in Table 2. Similar types of values were obtained at the DFT (B3LYP) level of approximation. From Table 2, we conclude that the cyclic complex $NaCl\cdots HNa$ shows the highest value of interaction energy, whereas NaCl•••H_2 exhibits the lowest value of binding energy. Moreover, the interaction energy in cyclic complexes is higher, indicating greater stability compared to linear structures. A similar trend has been reported previously as well for NaD(D=F and OH)···A-B complexes (Parajuli & Arunan, 2013). During our calculation, it was found that the binding energy with basis set superposition error correction is higher at the MP2 level of theory compared to the DFT (B3LYP) level of theory. (Supplementary Table S2). This is because MP2 calculates electron correlation energy, but DFT (B3LYP) calculates the total energy of the system in terms of the density of the electron.

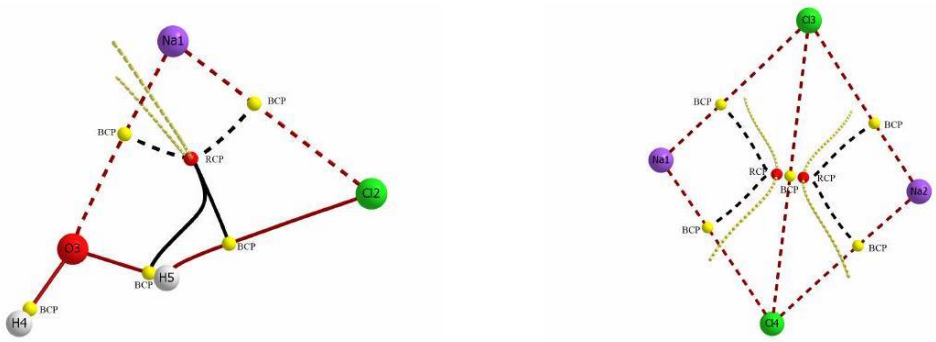

Figure 1. The optimized structure of the NaCl- H_20 complex and NaCl dimer in the MP2 level of theory using basis set Aug-CC-pVDZ (BCP and RCP represent the bond critical point and ring critical point respectively). The BCP has been shown in between all the atoms that are bonded

Table 1. Optimized ClNa···A-B bond distance (R_{Na-A}), change in Na-Cl distance (ΔR_{Na-Cl}), bond angles (∠ClNa···A), and Shift in ClNa···A-B frequency ($\Delta\upsilon$) of complexes with the basis set 6-311++G (d, p) and Aug-CC-pVDZ in MP2 level of theory

Complexes	6-311++ G (d, p)				Aug-CC-pVDZ			
	R_{Na-A}	ΔR_{Na-Cl}	∠ClNa···A	$\Delta\upsilon$	R_{Na-A}	ΔR_{Na-Cl}	∠ClNa···A	$\Delta\upsilon$
NaCl••• C_2H_4	2.840	0.010	172.12	-13.21	2.840	0.013	170.83	0.69
NaCl•••NH_3	2.483	0.024	179.45	15.85	2.483	0.026	179.25	13.03
NaCl•••H_2O	2.314	0.080	179.05	-35.63	2.314	0.085	178.44	-33.10
NaCl•••H_2	2.603	0.002	174.80	5.38	2.603	0.003	179.01	2.76
NaCl•••HNa	2.111	0.050	180.00	-14.99	2.111	0.058	180.00	-18.12
NaCl•••HLi	2.112	0.044	180.00	0.78	2.112	0.058	180.00	-1.35
NaCl•••FNa	2.078	0.054	180.00	8.96	2.078	0.194	180.00	-91.34
NaCl•••FLi	2.094	0.020	180.00	-50.62	2.094	0.031	180.00	-32.18

NaCl•••NaCl	2.595	0.020	180.00	-72.95	2.595	0.170	171.71	-71.73
NaCl•••HNa*	2.091	0.175	92.15		2.108	0.193	92.64	
NaCl•••HLi*	2.103	0.203	89.43		2.117	0.213	90.59	
NaCl•••FNa*	2.136	0.175	93.03		2.142	0.189	92.67	
NaCl•••FLi*	2.171	0.199	89.89		2.173	0.205	90.42	
NaCl•••NaCl*	2.539	0.157	79.35		2.595	0.170	78.29	

All the angles are in degree and distances are in Angstrom. Superscript '*' is for cyclic bounded complex

Table 2. Binding energy corrected for basis Set Superposition Error(E_b), zero-point vibrational energy (E_{zp}), and corrected binding energy (BE^{cor}) for complexes at the MP2 level of theory with a basis set $6-311++G(d,p)$ and Aug-CC-pVDZ.

Complexes	$6-311++G(d,p)$			Aug-CC-pVDZ		
	E_b	E_{zp}	BE^{cor}	E_b	E_{zp}	BE^{cor}
NaCl••• C_2H_4	-5.997	-7.230	-5.135	-6.401	-6.517	-5.685
NaCl•••NH_3	-15.352	-16.064	-13.754	-15.206	-14.353	-13.603
NaCl•••H_2O	-15.941	-16.480	-13.981	-16.425	-15.741	-14.596
NaCl•••H_2	-1.180	-0.497	-0.084	-1.317	-0.601	-0.2924
NaCl•••HF	-14.594	-14.197	-11.454	-16.337	-14.519	-13.315
NaCl•••HNa	-39.175	-39.047	-37.794	-41.010	-40.275	-39.737
NaCl•••HLi	-26.228	-25.784	-24.600	-22.979	-22.324	-21.505
NaCl•••FNa	-34.885	-35.743	-34.205	-52.154	-54.637	-51.201
NaCl•••FLi	-18.159	-18.806	-16.665	-18.805	-18.536	-17.422
NaCl•••NaCl	-43.901	-49.332	-27.396	-46.585	-46.993	-45.824
NaCl•••HNa*	-55.673	-57.777	-53.871	-58.834	-57.866	-57.097
NaCl•••HLi*	-49.552	-52.303	-47.167	-46.580	-45.729	-44.351
NaCl•••FNa*	-53.976	-57.519	-52.967	-42.242	-42.389	-41.269
NaCl•••FLi*	-48.664	-53.181	-47.333	-49.711	-50.256	-48.420
NaCl•••NaCl*	-43.901	-49.332	-43.105	-46.585	-46.993	-45.842

Superscript '*' is for the cyclic bounded complex.

Table 3. Topological analysis (electron density (ρ^c) and Laplacian of electron density ($\nabla^2\rho^c$) of complexes with basis set 6-311++G (d, p) and Aug-CC-pVDZ.

Complexes	$6-311++G(d,p)$		Aug-CC-pVDZ	
	ρ^c	$\nabla^2\rho^c$	ρ^c	$\nabla^2\rho^c$
NaCl•••C_2H_4	0.00978	0.04999	0.00868	0.03571
NaCl•••NH_3	0.01890	0.10859	0.01737	0.09683
NaCl•••H_2O	0.01898	0.13567	0.01855	0.12937
NaCl•••H_2	0.00616	0.03264	0.04713	0.02784
NaCl•••HF	0.01454	0.09688	0.01449	0.10923
NaCl•••HNa	0.01884	0.08207	0.01715	0.08347
NaCl•••HLi	0.01809	0.08063	0.01661	0.08202
NaCl•••FNa	0.03097	0.23110	0.03759	0.29028
NaCl•••FLi	0.02892	0.25491	0.02894	0.26491
NaCl•••NaCl	0.02354	0.12564	0.01931	0.11350
NaCl•••HNa*	0.02158	0.12015	0.01850	0.10682
NaCl•••HLi*	0.02022	0.11234	0.01770	0.10147
NaCl•••NaCl*	0.02238	0.12583	0.01932	0.11350
NaCl•••FNa*	0.02148	0.12016	0.01851	0.10769
NaCl•••FLi*	0.02031	0.11317	0.01790	0.10367

Superscript '*' is for cyclic bounded complex.

Table 4. Na-bonded radius for linear complexes in MP2 level of theory using basis sets $6-311++G(d,p)$ and Aug-CC-pVDZ, where R_{Na-B} is sodium bond radii and R_{A-B} is acceptor bond radii.

Complexes	6-311++ G (d, p)		Aug-CC-pVDZ	
	R_{Na-B}	R_{A-B}	R_{Na-B}	R_{A-B}
NaCl•••C_2H_4	1.1836	1.5922	1.1947	1.6496
NaCl•••NH_3	1.0599	1.3873	1.0726	1.4107
NaCl•••H_2O	1.0451	1.2539	1.0491	1.2664
NaCl•••H_2	1.1254	1.1942	1.1541	1.2412
NaCl•••HF	1.0783	1.3077	1.0692	1.3141
NaCl•••HNa	1.0755	1.0111	1.0800	1.0307
NaCl•••FNa	0.9789	1.1315	0.9489	1.1025
NaCl•••NaCl	1.0374	1.5019	1.0575	1.5379

AIM Topological Analysis

Another popular tool for analyzing intermolecular interactions is the theory of Atoms and Molecules (AIM), also known as the Quantum Theory of Atoms in Molecules (QTAIM) (Bader and Molecules, 1990). This analysis is also called topological analysis, as in this analysis the nature of chemical bonding is determined based on the presence of bond critical points (BCP) between the donor and acceptor atoms. Further, the values of electron density and Laplacian of the electron density at these bond critical points provide further insight into the nature of the bonding. For example, in the case of hydrogen bonding, there is a presence of BCP between a proton (H) donor and the acceptor. For this type of bonding, the electron density (ϱ) falls within the range of 0.002 to 0.040 atomic units, and the Laplacian of the electron density ($\nabla^2\varrho$) ranges from 0.024 to 0.139 atomic units (Koch and Popelier, 1995). In this study, we have computed (ρ) and $(\nabla^2\rho)$ to find out whether similar criteria can be applied to sodium bonds. For this, we compared our findings with previous reports. The value of computed (ρ) and $(\nabla^2\rho)$ at bond critical points in MP2 level of theory with the choice of the basis sets 6-311++G (d, p) and Aug-CC-pVDZ are presented in Table 3. These values of electron density range from 0.00978 to 0.03097 atomic units (au), and for the same level of theory, the range of Laplacian of electron density values varies from 0.04253 to 0.02541 au in the case of a linear structure for NaCl donors (Table 3). Similar ranges (electron density ranging from 0.0063 to 0.0264 and Laplacian of electron density ranging from 0.0324 to 0.2164) were documented in earlier work for NaF and NaH donors at the same level of theory (Parajuli & Arunan, 2013). The values of electron densities (ρ) were found to be similar for both linear and cyclic dimers. For example, in the linear NaCl dimer, the electron density is 0.02354 au whereas in the cyclic dimer, it is 0.02238 au. This is consistent with the cyclic dimer exhibiting stronger interactions than the linear dimer. Additionally, the Laplacian $(\nabla^2\rho)$ values for both systems are positive, indicating closed-shell interactions. Moreover, the value of electron density correlates with the binding energy. This type of correlation was also observed in earlier reports (Parajuli & Arunan, 2013).

The data for the DFT (B3LYP) level of theory were presented in supplementary results (Supplementary Table S3).

Na-bonded Radii from AIM Theoretical Analysis

Previously, the distance between the H atom and the H-A_BCP (H-bond radii) for various D-H···A complexes were derived from AIM analysis (Raghavendra et al, 2006). Thus, calculated H-bond radii show the range from the covalent radius (0.3Å) to Vander Waals radius (1.2Å). Similar types of work have also been performed in earlier reports (Parajuli and Arunan, 2013). The H-bond radii varied significantly with the dipole moment of the various donors going from the covalent radius (0.3Å) to Vander Waals radius (1.2Å). Therefore, we are interested in defining the Na-bond radii in a similar way. Our study shows that, unlike H-bond radii, the Na-bond radii have a smaller variance, ranging from 0.9489 Å to 1.1947 Å. Thus, the Na-bond radius is found to be close to the ionic bond radius (Raghavendra et al., 2013). The data for the DFT (B3LYP) level of theory were presented in supplementary results (Supplementary Table S4).

CONCLUSIONS

The first principles study of geometry, binding energy, the ZPVE, topological analysis, frequency shift, and bond radii of NaCl···A-B complexes has been performed in MP2 and DFT (B3LYP) level of calculations using different basis sets. ZPVE and BSSE are included in determining the accurate value of Binding Energy for all complexes, revealing more pronounced effects in strongly bound complexes. The frequency shift of Na-Cl stretching mode indicates that the frequency shift of Na-Cl stretching mode shows both red and blue shifts. Stationary points with one or more imaginary frequencies are observed in some structures, indicating that these linear structures are not favorable for these complexes.

Furthermore, Na-bond radii for Na-Cl show that sodium radii are closer to the ionic radii and are found to be smaller than Van der Waals radii. Additionally, Na-bond radio shows a smaller variation compared to hydrogen bond radii.

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AUTHOR CONTRIBUTIONS

BKC: Data curation, formal analysis, investigation, software, validation, visualization, writing original draft, review & editing; RP: Conceptualization, formal analysis, supervision, writing –review & editing, final approval.

CONFLICT OF INTEREST

The authors confirm that they have no conflicts of interest to disclose.

DATA AVAILABILITY STATEMENT

All supportive data will be made available by the corresponding author upon reasonable request.

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Supplementary Table S1. Optimized ClNa···A-B bond distance (R_{Na-A}), change in Na-Cl distance (ΔR_{Na-Cl}), bond angles (∠ ClNa···A-B), and Shift in ClNa···A-B frequency ($\Delta\upsilon$) of complexes with the basis set 6-311++G (d, p) and Aug-CC-pVDZ in DFT (B3LYP) level of theory

Complexes	6-311++ G (d, p)				A ug-CC-pVDZ			
	R_{Na-A}	ΔR_{Na-Cl}	$\angle ClNa\cdots A$	$\Delta\upsilon$	R_{Na-A}	ΔR_{Na-Cl}	$\angle ClNa\cdots A$	$\Delta\upsilon$
NaCl••• C_2H_4	2.778	0.016	176.24	-1.82	2.772	0.017	177.08	-3.56
NaCl•••NH_3	2.428	0.058	179.52	14.22	2.429	0.030	179.49	10.05
NaCl•••H_2O	2.242	0.086	170.69	-37.88	2.237	0.085	170.20	-36.83
NaCl•••H_2	2.510	0.004	176.02	3.81	2.564	0.004	174.37	2.95
NaCl•••HNa	2.068	0.056	180.00	-17.26	2.075	0.053	179.56	-21.74
NaCl•••HLi	2.064	0.052	180.00	-0.79	2.068	0.049	180.00	-9.89
NaCl•••FNa	2.096	0.063	180.00	11.46	2.100	0.061	180.00	10.09
NaCl•••FLi	2.122	0.051	180.00	33.78	2.117	0.052	178.88	34.79
NaCl•••NaCl	2.610	0.049	180.00	3.89	2.556	0.171	173.29	-70.76
NaCl•••HNa*	2.065	0.192	91.83		2.061	0.192	91.26	
NaCl•••HLi*	2.066	0.221	89.60		2.066	0.219	89.36	
NaCl•••FNa*	2.072	0.190	93.65		2.062	0.187	92.62	
NaCl•••FLi*	2.093	0.199	91.08		2.083	0.195	90.16	
NaCl•••NaCl*	2.553	0.170	77.66		2.555	0.170	76.76	

All the angles are in degree and distances are in Angstrom. Superscript '*' is for cyclic bounded complex

Supplementary Table S2. Binding energy corrected for basis Set Superposition Error(E_b), zero-point vibrational energy (E_{zp}), and corrected binding energy (BE^{cor}) for complexes with the basis set 6-311++G (d, p) and Aug-CC-pVDZ in DFT (B3LYP) level of theory

Complexes	$6-311++G(d,p)$			Aug-CC-pVDZ		
	E_b	E_{zp}	BE^{cor}	E_b	E_{zp}	BE^{cor}
NaCl••• C_2H_4	-5.740	-6.283	-6.492	-5.852	-6.436	-6.582
NaCl•••NH_3	-14.397	-15.566	-16.114	-13.992	-18.000	-15.666
NaCl•••H_2O	-15.498	-16.244	-17.291	-14.934	-15.540	-16.627
NaCl•••H_2	-0.356	-0.486	-1.395	-0.4623	-0.859	-1.445
NaCl•••HF	-8.401	-8.962	-8.937	-7.770	-8.253	-8.289
NaCl•••HNa	-22.203	-22.892	-23.827	-22.308	-22.808	-23.381
NaCl•••HLi	-21.219	-21.782	-22.905	-21.289	-21.979	-22.508
NaCl•••FNa	-33.187	-34.346	-33.887	-32.366	-33.204	-32.957
NaCl•••FLi	-16.665	-28.378	-28.119	-26.650	-22.641	-27.328
NaCl•••NaCl	-43.105	-22.090	-21.877	-45.208	-45.801	-45.969
NaCl•••HNa*	-39.239	-39.963	-41.014	- 39.578	-40.130	-41.323
NaCl•••HLi*	-45.246	-45.999	-47.509	- 45.179	-45.972	- 47.431
NaCl•••FNa*	-51.395	-52.449	-52.354	- 51.436	-52.292	- 52.397
NaCl•••FLi*	-49.096	-50.161	-50.360	- 49.150	-50.573	- 50.432
NaCl•••NaCl*	-44.323	-45.379	-45.076	- 45.210	-45.804	- 45.968

Superscript '*' is for the cyclic bounded complex.

Supplementary Table S3. Topological analysis (electron density (ρ^c) and Laplacian of electron density ($\nabla^2\rho^c$)) of complexes with the basis set 6-311++G (d, p) and Aug-CC-pVDZ in DFT (B3LYP) level of theory

Complexes	$6-311++G(d,p)$		Aug-CC-pVDZ	
	ρ^c	$\nabla^2\rho^c$	ρ^c	$\nabla^2\rho^c$
NaCl•••C_2H_4	0.01040	0.03861	0.01012	0.03963
NaCl•••NH_3	0.02058	0.11043	0.01970	0.10967
NaCl•••H_2O	0.02138	0.15617	0.02456	0.15896
NaCl•••H_2	0.00714	0.03216	0.05533	0.03019
NaCl•••HF	0.01711	0.12477	0.01660	0.12444
NaCl•••HNa	0.02003	0.07954	0.01828	0.08851
NaCl•••HLi	0.01978	0.08021	0.01828	0.08880
NaCl•••FNa	0.03234	0.23950	0.03131	0.23522
NaCl•••FLi	0.02977	0.21764	0.02937	0.22137
NaCl•••NaCl	0.01832	0.09538	0.02123	0.12403
NaCl•••HNa*	0.02155	0.10966	0.02038	0.11704
NaCl•••HLi*	0.02015	0.10220	0.01922	0.10879
NaCl•••FNa*	0.02154	0.11017	0.02046	0.11827
NaCl•••FLi*	0.02105	0.10810	0.02010	0.11637
NaCl•••NaCl*	0.02252	0.11623	0.02125	0.12428

superscript '*' is for cyclic bounded complex.

Supplementary Table S4. Na-bonded radius for linear complexes with the basis set 6-311++G (d, p) and Aug-CC-pVDZ in DFT (B3LYP) level of theory, where R_{Na-B} is sodium bond radii and R_{A-B} is acceptor bond radii

Complexes	6-311++ G (d, p)		Aug-CC-pVDZ	
	R_{Na-B}	R_{A-B}	R_{Na-B}	R_{A-B}
NaCl•••C_2H_4	1.1854	1.5920	1.1945	1.5203
NaCl•••NH_3	1.0600	1.3690	1.0579	1.3702
NaCl•••H_2O	1.0265	1.4110	1.0297	1.2139
NaCl•••H_2	1.1457	1.2105	1.1285	1.1739
NaCl•••HF	1.0629	1.2089	1.0668	1.1967
NaCl•••HNa	1.0743	1.0010	1.0792	0.9890
NaCl•••FNa	0.9783	1.1218	0.9742	1.1213
NaCl•••NaCl	1.0481	1.5081	1.0786	1.5310