Inorganic Cations

The $[NH_3Cl]^+$ Ion**

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Dedicated to Professor George Olah

Whereas at least seven simple inorganic cations, $[NH_3F]^+$,[1,2] $[NH_2F_2]^+$,[3] $[NF_4]^+$,[4] $[N_2F]^+$,[5] $[N_2F_3]^+$,[6] $[ONF_2]^+$,[7] and $[N_3NOF]^+$,[8] which contain N–F bonds, have been prepared and well characterized, the existence of corresponding N–Cl bond containing cations is not well established. Thus, only two N–Cl containing cations, $[NCl_4]^+$[9] and $[ONCl_2]^+$,[10,11] have been reported, however, our repeated attempts to duplicate their syntheses were unsuccessful, and the crystal structure, published for $[ONCl_2]^+[SbCl_6]^-$,[10] has been challenged on theoretical grounds.[12] The paucity of data on simple inorganic N–Cl containing cations can be attributed to the general explosiveness and instability of nitrogen chlorides.[13–15] Herein, the synthesis and characterization of $[NH_3Cl]^+M^-$ salts ($M = BF_4$, AsF_6, or SbF_6), the first examples of compounds containing a stable, simple inorganic cation with an N–Cl bond, are reported. To our knowledge, the formation of the $[NH_3Cl]^+$ ion has only been postulated based on investigations of aqueous solutions,[16] by theoretical calculations,[17] and by mass spectrometric studies.[17,18]

Without doubt, the most important member of the family of halogenamines is monochloramine, NH_2Cl. It is the crucial intermediate in the industrial synthesis of hydrazine.[13] Furthermore it is a very powerful disinfectant and germ killer.[14,19,20] Dilute aqueous solutions of NH_2Cl can conveniently be prepared by the chlorination of aqueous ammonia with hypochlorite.[13,14] However, the highest practical NH_2Cl concentration of these solutions is 97%, and purer compounds decompose extremely fast. At $-110\,°C$, NH_2Cl begins to melt with partial decomposition and, at $-40\,°C$, it decomposes continuously and often explosively, owing to the formation of ammonium chloride and more highly chlorinated products, such as NCl_3.[13] Therefore, the use of pure NH_2Cl is not feasible for the preparation of $[NH_3Cl]^+$ salts.

The handling problem of pure monochloramine was overcome by generating it at low temperature from $(Me_3Si)_2NCl$ and HF [Eq. (1)].

$$(Me_3Si)_2NCl + 2\,HF \rightarrow 2\,Me_3SiF + NH_2Cl \qquad (1)$$

The conversion of a $(R_3Si)_2N$ group into an H_2N group using a strong acid, such as CF_3COOH, has previously been demonstrated by Wiberg and co-workers for the syntheses of substituted tetrazenes.[21] When the reaction in Equation (1) is carried out in the presence of a strong Lewis acid, the $[NH_3Cl]^+$ salts are immediately formed, thus avoiding significant decomposition of NH_2Cl [Eq. (2)].

$$NH_2Cl + HF + M \rightarrow [NH_3Cl]^+[MF]^- \quad (M = BF_3,\ AsF_5,\ \text{or}\ SbF_5) \qquad (2)$$

The $[NH_3Cl]^+$ salts are formed in high yields, with small amounts of the corresponding $[NH_4]^+$ salts being the only impurities, which can be detected by vibrational or NMR spectroscopy. In one of our $[NH_3Cl]^+[BF_4]^-$ preparations, the formation of $[NH_4]^+[BF_4]^-$ as a by-product was also confirmed by its X-ray crystal structure. All attempts to obtain single crystals of the $[NH_3Cl]^+$ salts, suitable for a crystal-structure determination, failed. The formation of some $[NH_4]^+$ ions as a by-product is difficult to avoid because the acid-catalyzed decomposition of NH_2Cl starts already at $-110\,°C$. This observation is in accord with the report by Allenstein and Goubeau that neat solid NH_2Cl explodes on contact with BF_3 even at $-120\,°C$.[15]

All the $[NH_3Cl]^+$ salts, prepared in this study, are stable above room temperature. Unfortunately, reliable melting points could not be determined because of the $[NH_4]^+$ impurities. The salts readily dissolve in water with the

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formation of the corresponding oxonium salts and monochloramine. The monochloramine was identified by gas-phase IR spectroscopy and its characteristic intense smell [Eq. (3)].

$$[NH_3Cl]^+[MF]^- + H_2O \rightarrow [H_3O]^+[MF]^- + NH_2Cl \qquad (3)$$

The reaction in Equation (3) is in accord with the observation by Muench that even $(CH_3)_2NCl$, which is considerably more basic than NH_2Cl,[22] can be displaced from $[(CH_3)_2NClH]^+[CF_3SO_3]^-$ by water.[23] These displacement reactions are somewhat surprising because NH_2Cl possesses a higher gas-phase basicity (GB = 761 ± 5 kJ mol^{-1})[17b] than H_2O (GB = 691 kJ mol^{-1})[22] and, therefore, H_2O should not displace NH_2Cl from its $[NH_3Cl]^+$ salts. However, in aqueous solution or in solid–gas reactions, the relative basicities might be different. Unfortunately, the basicity of NH_2Cl in water is difficult to measure and, as yet, has not been reliably determined because of its instability in acidic solutions. Arguments have been presented that NH_2Cl should be either slightly more basic[17b,22,23] or more acidic than water.[23,24] That even in the case of the stronger base $(CH_3)_2NCl$, the displacement reactions with water proceed could be explained by the reaction in Equation (3) being an equilibrium which is shifted to the right by an excess of water and continuous removal of NH_2Cl owing to either its volatility or rapid decomposition. Equation (3) might also explain why, in the presence of water, protonation of NH_2Cl and formation of $[NH_3Cl]^+$ salts have not been observed. Although knowing the pK_a value of $[NH_3Cl]^+$ would be desirable, its experimental measurement would be very difficult because of the above problems and the unavoidable presence of $[NH_4]^+$ impurities.

The stability of the $[NH_3Cl]^+$ salts and their ability to generate NH_2Cl, when exposed to atmospheric moisture, make them ideally suited for NH_2Cl gas generation. This property could be exploited for a convenient gas-phase method of deactivating spores, such as anthrax.[25] Furthermore, previous work by Snyder and Margerum has indicated that the $[NH_3Cl]^+$ ion is a very reactive chlorinating agent for the transfer of chlorine to other amines, such as methylamine, amino acids, and peptides, while being a less reactive oxidant than Cl_2 or HOCl.[16c]

Conclusive evidence for the $[NH_3Cl]^+$ ion comes from the observed IR, Raman and NMR spectra and their comparison with theoretical calculations. To assess the accuracy of these calculations, we have tested these methods for isoelectronic CH_3Cl which is experimentally well characterized.[26] As can be seen from Table 1, the MP2 and CCSD(T) geometries deviate by less than 0.01 Å and 0.3° from the experimental values, while the B3LYP distances are, as expected, slightly longer. Therefore, we expect the geometry, predicted for $[NH_3Cl]^+$ (Table 1), to be also a good approximation of the true geometry of the free gaseous ion. Similarly, a comparison of the observed and calculated vibrational frequencies of CH_3Cl shows very good agreement (Table 2). Note, however, that the calculated frequencies are harmonic values for the free gas at 0 K, and that the experimentally observed frequencies require large anharmonicity corrections, particularly for the vibrations involving hydrogen atoms. Therefore, most of the differences between the observed and calculated frequencies can be attributed to anharmonicity effects, and the agreement between the harmonic values is much better.

Table 1: Calculated geometries of $[NH_3Cl]^+$, compared to observed[a] and calculated geometries of isoelectronic CH_3Cl.

	$[NH_3Cl]^+$				CH_3Cl			
	r(N-Cl) [Å]	r(N-H) [Å]	∢ H-N-Cl [°]	∢ H-N-H [°]	r(C-Cl) [Å]	r(C-H) [Å]	∢ H-C-Cl [°]	∢ H-C-H [°]
MP2/aug-cc-pvtz	1.735	1.025	109.2	109.8	1.780	1.084	108.4	110.6
CCSD(T)/aug-cc-pvtz	1.743	1.023	109.1	109.8	1.784	1.084	108.3	110.6
CCSD(T)/6-311++G(3df,3pd)[b]	1.747	1.026	109.3	109.7	–	–	–	–
B3LYP/aug-cc-pvtz	1.755	1.025	109.1	109.8	1.802	1.085	108.2	110.7
observed	–	–	–	–	1.776	1.085	108.6	110.4

[a] Data from ref. [26]. [b] Data from ref. [17b].

Table 2: Calculated harmonic and experimental anharmonic and harmonic vibrational frequencies and calculated IR and Raman intensities of CH_3Cl.[a]

Band		Calculated harmonic frequency			Experimental frequency	
		MP2	B3LYP	CCSD(T)	anharmonic	harmonic
A_1	ν_1	3111.2 (22) [150]	3071.0 (23) [155]	3098.5 (23)	2953.9	3088.4
	ν_2	1401.1 (11) [0.04]	1375.6 (12) [0.004]	1394.7 (12)	1354.9	1396.3
	ν_3	764.2 (24) [17]	707.3 (27) [17]	749.1 (22)	732.8	751.2
E	ν_4	3222.5 (4.6) [95]	3165.7 (7.9) [107]	3176.4 (7.8)	3039.3	3183.3
	ν_5	1511.0 (11) [7.5]	1482.8 (12) [7.7]	1510.2 (11)	1452.2	1496.2
	ν_6	1050.0 (4.0) [0.98]	1027.3 (4.1) [1.1]	1039.4 (3.5)	1018.1	1036.8

[a] For all calculations, the aug-cc-pvtz basis set was used; frequencies in cm^{-1}, IR and Raman intensities in km mol^{-1} and Å^4 amu^{-1}, respectively.

A comparison between the observed (Table 3 and Figure 1) and calculated vibrational frequencies of $[NH_3Cl]^+$ is given in Table 4. The differences between the observed anharmonic and the calculated harmonic frequencies are comparable to those in CH_3Cl and establish the new species as the $[NH_3Cl]^+$ ion. The slight variation in the observed vibrational frequencies of the $[NH_3Cl]^+$ ion in the different salts is attributed to solid-state effects, such as various degrees of anion–cation interactions and hydrogen bonding. Further support for the presence of the $[NH_3Cl]^+$ ion comes from the ^{35}Cl–^{37}Cl isotopic shift of the N–Cl stretching vibration. The N–Cl stretching vibration (Figure 1) shows a splitting of approximately 6 cm^{-1}, in accord with the calculated harmonic

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Table 3: Observed vibrational spectra[a] of solid $[NH_3Cl]^+ M^-$ ($M = BF_4$, AsF_6, SbF_6) and their assignments.

$[NH_3Cl]^+[BF_4]^-$		$[NH_3Cl]^+[AsF_6]^-$		$[NH_3Cl]^+[SbF_6]^-$		$[NH_3Cl]^+$ (C_{3v})	M^-	
Raman	IR	Raman	IR	Raman	IR		$[BF_4]^-$ (T_d)	$[AsF_6]^-$ $[SbF_6]^-$ (O_h)
3247.6(18)	3221vw	3241.2(16)	3209w	3229.6(8)	3217vw	ν_4 (E)		
3188.6(9)		3167.7(3)	3172w	3168.0(4)	3112vw	ν_1 (A_1)		
1552.2(1)	1570w	1566.7(0+)	1564w	1557.0(0+)	1569w	ν_5 (E)		
1454.8(0+)	1458m	1447.0(0+)	1435s	1433.5(0+)	1435s	ν_2 (A_1)		
n.o.	n.o.	1071.0(0+)	1071w	1068.8(0+)	1072m	ν_6 (E)		
759.0(82)	763w	766.4(15)	[b]	766.2(49)	767w	ν_3 ^{35}Cl (A_1)		
753.8(50)		761.2(9)	[b]	761.2(30)	762w	ν_3 ^{37}Cl (A_1)		
1079.0(0+)	1035vs,vb						$\tilde{\nu}_3$ (F_2)	
772.0(100)	769w						$\tilde{\nu}_1$ (A_1)	
			703vs,b		659vs			$\tilde{\nu}_3$ (F_{1u})
		688.6(100)		654.4(100)				$\tilde{\nu}_1$ (A_{1g})
		573.8(22)		570.1(28)				$\tilde{\nu}_2$ (E_g)
528.8(14)	530/524m						$\tilde{\nu}_4$ (F_2)	
354.5(18)							$\tilde{\nu}_2$ (E)	
		373.0(43)		281.6(38)				$\tilde{\nu}_5$ (F_{2g})

[a] Frequencies in cm^{-1} and uncorrected relative intensities. [b] Observed as shoulders on the very intense 703 cm^{-1} band; n.o. = not observed.

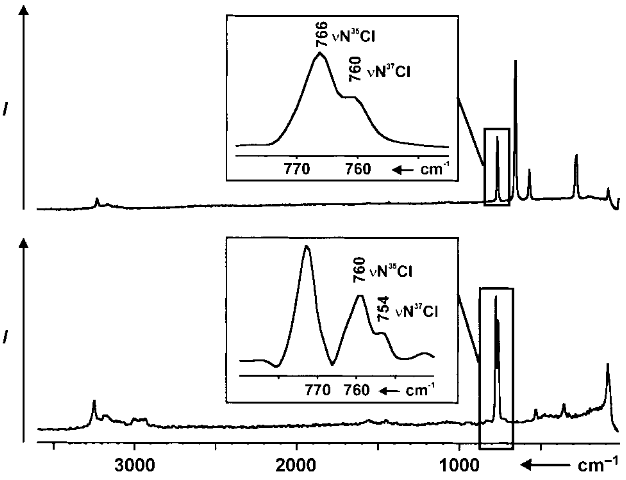

Figure 1. Raman spectra of $[NH_3Cl]^+[SbF_6]^-$ (upper) and $[NH_3Cl]^+[BF_4]^-$ (lower). The enlarged sections of the spectra show a 35/37 chlorine isotopic splitting in the N–Cl vibration.

splittings, ranging from 6.6 (B3LYP) to 7.1 (MP2) cm^{-1}. If the observed isotopic shifts were corrected for anharmonicity, the agreement would be even better. In CH_3Cl, anharmonicity corrections increase the observed ^{35}Cl–^{37}Cl isotopic shift by 0.29 cm^{-1} from the anharmonic value, $\Delta\nu = 5.83$, to the harmonic value, $\Delta\omega = 6.12$ cm^{-1}.[26] The complexity of the Raman bands of $[NH_3Cl]^+[BF_4]^-$ in the region of the N–H stretching modes (Figure 1) can be explained by Fermi resonance between $\nu_1(A_1)$ and $2\nu_5(A_1)$ and the possible presence of some $[NH_4]^+$ impurity.

Additional support for the $[NH_3Cl]^+$ ion comes from the results of a normal coordinate analysis (Table 5). The general harmonic force field, calculated for the $[NH_3Cl]^+$ ion at the CCSD(T) level, corresponds very closely to that of isoelectronic CH_3Cl.[25] All vibrations are highly characteristic, and only the N–Cl stretching vibration mixes, as expected, to a small extent with the NH_3 umbrella deformation mode.

The ^{14}N and ^{1}H NMR spectra of $[NH_3Cl]^+[SbF_6]^-$ in HF and DF solutions (Table 6) exhibit single resonances at $\delta = -364$ and 7.91 ppm, respectively. The observed chemical shifts are in good agreement with our expectations for the $[NH_3Cl]^+$ ion: the nitrogen atom in the $[NH_3Cl]^+$ ion is slightly deshielded compared with that in $[NH_4]^+$ ($\delta = -367$ ppm), but significantly more shielded than that in $[NH_3F]^+$ ($\delta = -252.1$ ppm).[27] The proton shift ($\delta = 7.91$ ppm) falls in between those of the $[NH_4]^+$ ($\delta = 5.71$ ppm) and $[NH_3F]^+$ ($\delta = 10.4$ ppm) ions.[2] The similarity of the ^{14}N shifts of the $[NH_3Cl]^+$ and $[NH_4]^+$ ions cannot be attributed to signal averaging between the $[NH_3Cl]^+$ ion and either the $[NH_4]^+$ ion or the solvents, because in all spectra separate signals were observed for the $[NH_3Cl]^+$ and

Table 4: Calculated harmonic and experimental anharmonic vibrational frequencies and calculated IR and Raman intensities of $[NH_3Cl]^+$.[a]

Band		Calculated harmonic frequency				Range of experimental anharmonic frequency
		MP2	B3LYP	CCSD(T)		
				aug-cc-pvtz	6-31++G(3df,3pd)[b]	
A_1	ν_1	3374.7 (85) [87]	3357.1 (79) [91]	3404.1 (78)	3355.1	3112–3188
	ν_2	1475.9 (59) [0.48]	1466.5 (57) [0.45]	1474.0 (56)	1467.9	1435–1458
	ν_3	785.0 (2.6) [12]	737.5 (2.4) [13]	762.9 (2.1)	741.5	759–767
E	ν_4	3480.6 (386) [42]	3445.0 (356) [47]	3484.1 (349)	3441.9	3209–3247
	ν_5	1642.1 (101) [6.1]	1628.9 (105) [6.5]	1646.7 (100)	1628.8	1552–1570
	ν_6	1054.8 (37) [1.35]	1037.0 (36) [1.69]	1045.8 (35)	1039.2	1069–1072

[a] For the MP2 and B3LYP calculations, the aug-cc-pvtz basis set was used; frequencies in cm^{-1}, intensities (infrared) and [Raman] in km mol^{-1} and Å^4 amu^{-1}, respectively. [b] Data from ref. [17b].

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Table 5: General harmonic force field[a] of C_{3v} $[NH_3Cl]^+$ and potential energy distribution[b] calculated at the CCSD(T)/aug-cc-pvtz level of theory.

Band		Approximate mode description	Frequency [cm^{-1}]	Symmetry force constants				PED
					F_{11}	F_{22}	F_{33}	
A_1	ν_1	ν sym NH_3	3404.1	F_{11}	6.746	0.138	0.100	99.6 (1)
	ν_2	δ sym NH_3	1474.0	F_{22}		0.619	−0.454	99.7 (2)
	ν_3	ν N–Cl	762.9	F_{33}			3.997	86.3 (3) + 13.7 (2)
					F_{44}	F_{55}	F_{66}	
E	ν_4	ν asym NH_3	3484.1	F_{44}	6.591	−0.136	0.000	98.3 (4)
	ν_5	δ asym NH_3	1646.7	F_{55}		0.610	−0.011	95.3 (5)
	ν_6	δ wag NH_3	1045.8	F_{66}			0.668	95.2 (6)

[a] Stretching constants in mdyn Å^{-1}, deformation constants in mdyn Å/rad^2, and stretch-bend interaction constants in mdyn/rad. [b] PED in percent. Symmetry coordinates contributing less than 5 % are omitted. Symmetry coordinates, taken from ref.[26], are defined as follows: $S_1 = \nu$ sym (N-H), $S_2 = \delta$ sym (H-N-H–H-N-Cl), $S_3 = \nu$ (N-Cl), $S_4 = \nu$ asym (N-H), $S_5 = \delta$ asym (H-N-H), $S_6 = \delta$ asym (Cl-N-H).

Table 6: Observed NMR spectra of HF/DF solutions of $[NH_3Cl]^+[SbF_6]^-$.[a]

Solvent, *T*	Chemical shift [ppm] (line width [Hz]) δ^{14}N	δ^{1}H
HF, 20 °C	−363 (188)	[b]
DF, 20 °C	−364 (125)	7.91 (3.8)

[a] In addition to the resonances arising from the $[NH_3Cl]^+$ ion, δ^{14}N resonance signals arising from the $[NH_4]^+$ ion were observed at −368 (q, 54.7 Hz) in HF and at −367 (q, 54.8 Hz) ppm in DF; the δ^{1}H resonance signals from the $[NH_4]^+$ ion were observed at 5.65 (tr, 54.6 Hz) in HF and at 5.71 (tr, 54.4 Hz) ppm in DF. [b] Resonance obscured by the HF solvent signal.

$[NH_4]^+$ ions which were always separated by the same amount, and the $[NH_4]^+$ ion proton resonance consisted of very narrow triplets of equal intensity arising from ^{14}N–^{1}H spin–spin coupling. The similarity of the ^{14}N shifts in the $[NH_4]^+$ and $[NH_3Cl]^+$ ions is attributed to nitrogen and chlorine having very similar electronegativities, resulting in a low polarity of the N–Cl bond and a weak electron-withdrawing effect of chlorine. In contrast, substitution of one hydrogen atom by a highly electronegative fluorine atom results in strong deshielding of the nitrogen atom. A similar trend is also reflected, although to a lesser degree, in the ^{13}C shifts of CH_4 ($\delta = -2.1$ ppm), CH_3Cl ($\delta = 25.6$ ppm), and CH_3F ($\delta = 71.6$ ppm).[28]

In summary, this study provides $[NH_3Cl]^+$, the first stable, simple, inorganic cation containing an N–Cl bond. For the syntheses of the $[NH_3Cl]^+$ salts, the explosiveness and thermal instability of the parent molecule NH_2Cl was circumvented by using a safe organosilicon derivative, $(R_3Si)_2NCl$, as a precursor. Conclusive evidence for the existence of the $[NH_3Cl]^+$ ion is given by its vibrational and NMR spectra and theoretical calculations.

Experimental Section

Caution! *Neat chloramines are highly unstable and often can decompose explosively. They should be handled on a small scale with appropriate safety precautions.*

All reactions were carried out in Teflon–FEP (FEP = perfluoro ethylene propylene polymer) ampules that contained Teflon-coated magnetic stirring bars and were closed by stainless steel valves. Volatile materials were handled on a stainless steel vacuum line. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box. IR spectra were recorded on a Midac, M Series, FT-IR spectrometer using AgCl pellets. The pellets were prepared inside the glove box using an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm with power levels of 800 mW or less. Pyrex melting point capillaries, glass NMR or 9 mm Teflon–FEP tubes were used as sample containers. NMR spectra were recorded unlocked on a Bruker AMX 500 NMR spectrometer at room temperature. The ^{14}N and ^{1}H NMR spectra were referenced to external samples of neat nitromethane and tetramethylsilane in $CDCl_3$, respectively.

The $(Me_3Si)_2NCl$ starting material was prepared from $(Me_3Si)_2NH$ and *t*BuOCl using a literature method.[29] The HF/DF solvents (Matheson Co./Ozark Mahoning) were dried[30] by storage over BiF_5 (Ozark Mahoning). SbF_5 (Ozark Mahoning) was purified by distillation prior to use. BF_3 (Matheson) and AsF_5 (Ozark Mahoning) were used as received.

$[NH_3Cl]^+M^-$ [M = BF_4, AsF_6, SbF_6]: In a typical experiment, anhydrous HF (2 mL of liquid) and BF_3, AsF_5, or SbF_5 (1.44 to 3.176 mmol) were combined at −196 °C in a 9 mm Teflon–FEP ampule closed by a stainless steel valve. The mixture was warmed to 25 °C and then recooled to −196 °C. A stoichiometric amount of $(Me_3Si)_2NCl$ was added to the ampule at −196 °C, and additional HF was condensed on top of it at a very slow rate to avoid contact of the frozen silyl compound with liquid HF during the condensation process. The frozen mixture was warmed first to −78 °C and then slowly to 25 °C. During warm-up, a colorless precipitate was formed, which was only partially soluble in the HF. The ampule was immediately recooled to −64 °C and all volatiles were pumped off at this temperature. Colorless stable solids of $[NH_3Cl]^+[BF_4]^-$, $[NH_3Cl]^+[AsF_6]^-$, or $[NH_3Cl]^+[SbF_6]^-$ were left behind which contained small amounts of the corresponding $[NH_4]^+$ salts as the only impurities, detectable by vibrational spectroscopy.

Theoretical calculations were performed using the GAMESS,[31] Gaussian 98,[32] and ACES II[33] program systems, and the augmented correlation-consistent polarized vvalence triple-zeta basis set (aug-cc-pvtz) of Dunning et al.[34] Computational methods included density functional theory with the hybrid B3LYP functional,[35] second order perturbation theory (MP2, also known as MBPD(2))[36] and coupled-cluster singles and doubles[37] with perturbative estimates of triple excitations (CCSD(T)).[38]

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