The NH_3Cl^+ Cation[**,†]

Stefan Schneider, Ralf Haiges, Thorsten Schroer, Jerry Boatz, and Karl O. Christe**

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 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] In this paper, 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

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Whereas at least seven simple inorganic cations, NH3F+,[1,2] NH2F2+,[3] NF4+,[4] N2F+,[5] N2F3+,[6] ONF2+,[7] and N3NOF+,[8] which contain N-F bonds, have been prepared and well characterized, the existence of corresponding N-Cl containing cations is not well established. Thus, only two N-Cl containing cations, NCl4+[9] and ONCl2+,[10,11] have been reported, however, our repeated attempts to duplicate their syntheses were unsuccessful, and the crystal structure, published for ONCl2+SbCl6-,[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] In this paper, the synthesis and characterization of NH3Cl+M- salts (M = BF4, AsF6, or SbF6), the first examples of compounds containing a stable, simple inorganic

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cation with an N-Cl bond, are reported. To our knowledge, the formation of the NH_3Cl^+ cation has only been postulated based on investigations of aqueous solutions,[16] by theoretical calculations,[17] and by mass spectrometry 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, due 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)].

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

When the reaction 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)].

$$NH_2Cl + HF + M \longrightarrow NH_3Cl^+MF^- \ (M = BF_3,\ AsF_5,\ or\ SbF_5) \qquad (2)$$

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^+ as by-product is difficult to avoid because the decomposition of NH_2Cl starts already at -110 °C.

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

$$NH_3Cl^+MF^- + H_2O \longrightarrow H_3O^+MF^- + NH_2Cl \qquad (3)$$

Reaction (3) shows that H_2O is a stronger base than NH_2Cl, and that NH_3Cl^+ can protonate H_2O. This also explains why, in the presence of water, protonation of NH_2Cl and formation of NH_3Cl^+ salts are not observed. These conclusions differ from those, reached by Ricci and Rosi, that NH_3Cl^+ does not protonate water.[17] The stability of the NH_3Cl^+ salts and their ability to generate NH_2Cl, when exposed to atmospheric moisture, make them ideal NH_2Cl gas generators. This property could be exploited for a convenient gas-phase method of deactivating spores, such as anthrax.[21]

Conclusive evidence for the NH_3Cl^+ cation comes from the observed infrared, 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.[22] 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). It must be kept in mind, 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 among the harmonic values is excellent.

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 NH_3Cl^+. The slight variation in the observed vibrational frequencies of NH_3Cl^+ 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 NH_3Cl^+ 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 ~ 6 cm^{-1}, in accord with the calculated harmonic 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 ?? = 5.83 to ?? = 6.12 cm^{-1}.[22] 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 $?_1(A_1)$ and $2?_5(A_1)$ and the possible presence of some NH_4^+ impurity.

Additional support for NH_3Cl^+ comes from the results of a normal coordinate analysis (Table 5). The general harmonic force field, calculated for NH_3Cl^+ at the CCSD(T) level, corresponds very closely to that of isoelectronic CH_3Cl.[22] 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-364 and 7.91 ppm, respectively. The observed chemical shifts are in good agreement with our expectations for NH_3Cl^+. The nitrogen atom in NH_3Cl^+ is slightly deshielded from that in NH_4^+ (-367 ppm), but significantly more shielded than that in NH_3F^+ (-252.1 ppm).[23] The proton shift (7.91 ppm) falls in between those of NH_4^+ (ppm) and NH_3F^+ (10.4 ppm).[2]

In conclusion, this study provides with 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 NH_3Cl^+ is provided by its vibrational and NMR spectra and theoretical calculations.

Experimental Section

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

Materials and Apparatus. All reactions were carried out in Teflon-FEP 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. Infrared 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.[24] The HF/DF solvents (Matheson Co./Ozark Mahoning) were dried 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.

Preparation of $NH_3Cl^+M^-$ [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 phase. 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 volatiles were pumped off, leaving behind colorless stable solids of $NH_3Cl^+BF_4^-$, $NH_3Cl^+AsF_6^-$, or $NH_3Cl^+SbF_6^-$, respectively, containing small amounts of the corresponding NH_4^+ salts as the only impurities detectable by vibrational spectroscopy.

Theoretical Calculations. Theoretical calculations were carried out on IBM RS/6000 work stations using the GAMESS,[25] Gaussian 98,[26] and ACES II[27] program systems, an aug-cc-pvtz basis set,[28] and the density functional B3LYP,[29] and the correlated MP2[30] and single-

and double-excitation coupled cluster methods,[31] including a non-iterative treatment of connected triple excitations.[32]

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References

[1] (a) V. Grakauskas, A. H. Remanick, K. Baum, *J. Am. Chem. Soc.* **1968,** *90,* 3839; (b) V. Grakauskas, *J. Inorg. Nucl. Chem.***1973,** *35,* 3034.

[2] (a) R. Minkwitz, R. Nass, *Z. Naturforsch.* **1982,** *37b,* 1558; (b) R. Minkwitz, A. Liedtke, R. Nass, *J. Fluorine Chem.* **1987,** *35,* 307.

[3] K. O. Christe, *Inorg. Chem.* **1975**, *14,* 2821.

[4] (a) K. O. Christe, J.P. Guertin, A.E. Pavlath, *Inorg. Nucl. Chem. Letters* **1966**, *2*, 83; (b) I. V. Nikitin, V. Ya. Rosolovskii, *Russ. Chem. Rev.***1985,** *54,* 426.

[5] (a) D. Moy, A. R. Young, *J. Am. Chem. Soc.* **1965,** *87,* 1889; (b) J. K. Ruff, *Inorg. Chem.* **1966**, *5*, 1791; (c) H. W. Roesky, O. Glemser, D. Bormann, *Chem. Ber.* **1966,** *99,* 1589; (d) A. V. Pankratov, N. I. Savenkova, *Russ. J. Inorg. Chem.* **1968,** *13,* 1345; (e) J. Shamir, J. Binenboym, *J. Mol. Struct.* **1969,** *4,* 100; (e) K. O. Christe, R. D. Wilson, W.

Sawodny, *J. Mol. Struct.* **1971,** *8,* 245; (f) K. O. Christe, R. D. Wilson, W. W. Wilson, R. Bau, S. Sukumar, D. A. Dixon, *J. Am. Chem. Soc.* **1991,** *113,* 3795.

[6] (a) J. K. Ruff, *J. Am. Chem. Soc.* **1965,** *87,* 1140; J. K. Ruff, *Inorg. Chem.* **1966**, *5,* 1791; (c) A. R. Young, D. Moy, *Inorg. Chem.* **1967**, *6,* 178; (d) E. W. Lawless, *Anal. Lett*. **1967,** *1,* 153; A. M. Qureshi, F. Aubke, *Can. J. Chem.* **1970,** *48,* 3117; K. O. Christe, C. J. Schack, *Inorg. Chem.* **1978**, *17,* 2749.

[7] (a) W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornik, C. A. Wamser, J. R. Holmes, R. E. Eibeck, B. B. Stewart, *J. Am. Chem. Soc.* **1966,** *88,* 2604; (b) K. O. Christe, W. Maya, *Inorg. Chem.* **1969**, *8*, 1253; (c) C. A. Wamser, W. B. Fox, B. Sukornik, J. R. Holmes, B. B. Stewart, R. Juurick, N. Vanderkooi, D. Gould, *Inorg. Chem.* **1969**, *8*, 1249; (d) K. O. Christe, J. F. Hon, D. Pilipovich, *Inorg. Chem.* **1973**, *12*, 84; (e) J. Mason, K. O. Christe, *Inorg. Chem.* **1983**, *22*, 1849; (f) F. Cacace, F. Pepi, *J. Phys. Chem.***1994,** *98,* 8009; (f) R. J. Gillespie, E. A. Robinson, G. L. Heard, *Inorg. Chem.* **1998**, *37*, 6884; (g) A. Vij, X. Zhang, K. O. Christe, *Inorg. Chem.* **2001**, *40*, 416.

[8] W. W. Wilson, K. O. Christe, H. Willner, J. A. Boatz, A. Vij, V. Vij, paper 449, presented at the 225th National ACS Meeting, New Orleans, LA, 24 March, 2003.

[9] R. Minkwitz, D. Bernstein, W. Sawodny, *Angew. Chem. Int. Ed.* **1990**, *29*, 181.

[10] K. Dehnicke, H. Aeissen, M. Koelmel, J. Straehle, *Angew. Chem.* **1977**, *89*, 569.

[11] R. Minkwitz, D. Bernstein, W.Sawodny, H. Haertner, *Z. Anorg. Allg. Chem.*, **1990**, *580*, 109.

[12] (a) M. Brumm, G. Frenking, W. Koch, *Chem. Phys. Lett.* **1991,** *182*, 310*;* (b) M. Brumm, G. Frenking, J. Breidung, W. Thiel, *Chem. Phys. Lett.* **1992,** *197*, 330.

[13] J. Jander, U. Engelhardt, in *Developments in Inorganic Nitrogen Chemistry* (Ed.: C. B. Colburn) Elsevier Scientific Publishing Company, Amsterdam, London, New York, **1973**, p. 70.

[14] A. F. Holleman, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, Berlin, New York, **1995**, p. 678.

[15] E. Allenstein, J. Goubeau, *Z. Anorg. Allg*. *Chem.*, **1963**, *322*, 145.

[16] See for example: (a) P. K. Wrona, *J. Electroanal. Chem.*, **1998**, *453*, 197; (b) M. Elkhatib, A. Marchand, L. Peyrot, J. J. Counioux, H. Delalu, *Int. J. Chem. Kinet*., **1997**, *29*, 89; (c) M. P. Snyder, D. W. Margerum, *Inorg. Chem.*, **1982**, *21*, 2545; (d) E. T. Gray, Jr., D. W. Margerum, R. P. Huffmann, in *Organometals and Organometalloids, Occurence and Fate in the Environment*, (Eds.: F. E. Brinkmann, J. M. Bellama) American Chemical Society: Washington D.C., **1978**; ACS Symp. Ser. No. 82, p. 264.

[17] (a) R. K. Millburn, C. F. Rodriquez, A. C. Hopkinson, *J. Phys. Chem. B*, **1997**, *101*, 1837; (b) A, Ricci, M. Rosi, *J. Phys. Chem. A.*, **1998**, *102*, 10189.

[18] T. Kotiaho, B. J. Shay, R. G. Cooks, M. N. Eberlin, *J. Am. Chem. Soc.*, **1993**, *115*, 1004; and references citied therein.

[19] W. Gerhartz, Ed., *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Edition, Vol. A6, VCH Verlagsgesellschaft mbH Weinheim, p. 533.

[20] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press: Oxford, 1984.

[21] (a) S. W. Chensue, *Am. J. Pathol.* **2003,** *163,* 1699; (b) M. J. Rosowitz, S. H. Leppla, *Nature,* **2002,** *418,* 825 ; (c) K. Brown, *Science,* **2001,** *294,* 1813.

[22] G. M. Black, M. M. Law, *J. Mol. Spectrosc.* **2001,** *205,* 280, and references cited therein.

[23] J. Mason, K. O. Christe, *Inorg. Chem.* **1983**, *22,* 1849.

[24] N. Wiberg, F. Raschig, *J. Organometal. Chem.*, **1967**, *10*, 15.

[25] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comp. Chem.* **1993**, *14*, 1347.

[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Jr. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, R. E. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Peterson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

[27] J. F.Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balkova, D. E. Bernholdt, K. K. Baeck, P. Rozyczko, H. Sekino, C. Hober, R. J. Bartlett, *ACES II, Quantum Theory Project*; University of Florida: Integral packages included are VMOL (J. Almlof, P. R. Taylor,),

BPROPS (P. R. Taylor), and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jorgensen, J. Olsen, P. R. Taylor).

[28] (a) T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007; (b) R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796; (c) D. E. Woon, T. H. Dunning, Jr., *J. Chem. Phys.* **1993**, *98*, 1358.

[29] The B3LYP functional uses a three-parameter exchange functional of Becke (B3) [A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; P. J. StephensC. F. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623] and the Lee, Yang, and Parr (LYP) correlation gradient-corrected functional [C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785].

[30] (a) J. A. Pople, J. S. Binkley, R. Seeger, *Int. Quantum Chem.* **1976**, *10*, 1; (b) R. J. Bartlett, D. M. Silver, *Int. Quantum Chem.* **1975**, *9*, 183; (c) M. Dupuis, S. Chin, A. Marquez in: Relativistic and Electron Correlation Effects in Molecules, (Ed.: G. Malli) Plenum, New York, 1994; (d) M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem. Phys. Lett*. **1990**, *166*, 275; (e) R. J. Bartlett, R. J. Stanton, Applications of post-Hartree-Fock methods: A Tutorial, in: Reviews of Computational Chemistry, Vol. V, K. B. Lipkowitz, (Ed.: D. B. Boyd), VCH Publishers, New York, 1994.

[31] G. D. III.Purvis, R. J. Bartlett, *J. Chem. Phys.* **1982**, *76*, 1910.

[32] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.

Table 1. Calculated geometries (Å, °) of NH_3Cl^+, compared to observed[a] and calculated geometries of isoelectronic CH_3Cl.

	NH_3Cl^+				CH_3Cl			
	r (N-Cl)	r (N-H)	< H-N-Cl	< H-N-H	r (C-Cl)	r (C-H)	< 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 [22]. [b] Data from ref [17(b)].

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

		calculated harmonic freq,			experimental freq,	
		MP2	B3LYP	CCSD(T)	anharmonic	harmonic
A_1	$?_1$	3111.2 (22) [150]	3071.0 (23) [155]	3098.5 (23)	2953.9	3088.4
	$?_2$	1401.1 (11) [0.04]	1375.6 (12) [0.004]	1394.7 (12)	1354.9	1396.3
	$?_3$	764.2 (24) [17]	707.3 (27) [17]	749.1 (22)	732.8	751.2
E	$?_4$	3222.5 (4.6) [95]	3165.7 (7.9) [107]	3176.4 (7.8)	3039.3	3183.3
	$?_5$	1511.0 (11) [7.5]	1482.8 (12) [7.7]	1510.2 (11)	1452.2	1496.2
	$?_6$	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}, infrared and Raman intensities in km/mol and $Å^4$/amu, respectively.

Table3. 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	?$_5$ (E)		
1454.8(0+)	1458m	1447.0(0+)	1435s	1433.5(0+)	1435s	?$_2$ (A_1)		
n.obsd.	n.obsd.	1071.0(0+)	1071w	1068.8(0+)	1072m	?$_6$ (E)		
759.0(82)	763w	766.4(15)	[b]	766.2(49)	767w	$\nu_3{}^{35}$Cl (A_1)		
753.8(50)		761.2(9)	[b]	761.2(30)	762w	$\nu_3{}^{37}$Cl (A_1)		
1079.0(0+)	1035vs,vb						ν_3 (F_2)	
772.0(100)	769w						ν_1 (A_1)	
			703vs,b		659vs			ν_3 (F_{1u})
		688.6(100)		654.4(100)				ν_1 (A_{1g})
		573.8(22)		570.1(28)				ν_2 (E_g)
528.8(14)	530/524m						ν_4 (F_2)	
354.5(18)							ν_2 (E)	
		373.0(43)		281.6(38)				?$_5$ (F_{2g})

[a] Frequencies in cm^{-1} and uncorrected relative intensities.[b] Observed as shoulders on the very intense 703 cm^{-1} band.

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

		calculated harmonic freq,				
				CCSD(T)		range of experimental
		MP2	B3LYP	aug-cc-pvtz	6-31++G(3df,3pd)[b]	anharmonic freq
A_1	$?_1$	3374.7 (85) [87]	3357.1 (79) [91]	3404.1 (78)	3355.1	3112 - 3188
	$?_2$	1475.9 (59) [0.48]	1466.5 (57) [0.45]	1474.0 (56)	1467.9	1435 - 1458
	$?_3$	785.0 (2.6) [12]	737.5 (2.4) [13]	762.9 (2.1)	741.5	759 - 767
E	$?_4$	3480.6 (386) [42]	3445.0 (356) [47]	3484.1 (349)	3441.9	3209 - 3247
	$?_5$	1642.1 (101) [6.1]	1628.9 (105) [6.5]	1646.7 (100)	1628.8	1552 - 1570
	$?_6$	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} (infrared) and [Raman] intensities in km/mol and $Å^4$/amu, respectively. [b] Data from ref [17(b)].

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.

		approx mode description	freq, cm^{-1}		symmetry force constants			PED
					F_{11}	F_{22}	F_{33}	
A_1	$?_1$	? sym NH_3	3404.1	F_{11}	6.746	0.138	0.100	99.6 (1)
	$?_2$	d sym NH_3	1474.0	F_{22}		0.619	-0.454	99.7 (2)
	$?_3$	? N - Cl	762.9	F_{33}			3.997	86.3 (3) + 13.7 (2)
					F_{44}	F_{55}	F_{66}	
E	$?_4$	? asym NH_3	3484.1	F_{44}	6.591	-0.136	0.000	98.3 (4)
	$?_5$	d asym NH_3	1646.7	F_{55}		0.610	-0.011	95.3 (5)
	$?_6$	d wag NH_3	1045.8	F_{66}			0.668	95.2 (6)

[a] Stretching constants in mdyn/Å, deformation constants in mdynÅ/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. [22], are defined as follows: S_1 = ? sym (N-H), S_2 = d sym (H-N-H – H-N-Cl), S_3 = ? (N – Cl), S_4 = ? asym (N-H), S_5 = d asym (H-N-H), S_6 = d asym (Cl-N-H).

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

solvent, temp	chem shift, ppm (line width, Hz) d ^{14}N	d ^{1}H
HF, 20 °C	-363 (188)	[a]
DF, 20 °C	-364 (125)	7.91 (3.8)

[a] Resonance obscured by the HF solvent peak. [b] In addition to the resonances due to NH_3Cl^+, d ^{14}N signals due to NH_4^+ were observed at -368 (q, 54.7 Hz) in HF and at -367 (q, 54.8 Hz) in DF; the d ^{1}H signals due to NH_4^+ were observed at 5.65 (tr, 54.6 Hz) in HF and at 5.71 (tr, 54.4 Hz) in DF.

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 NCl vibration.

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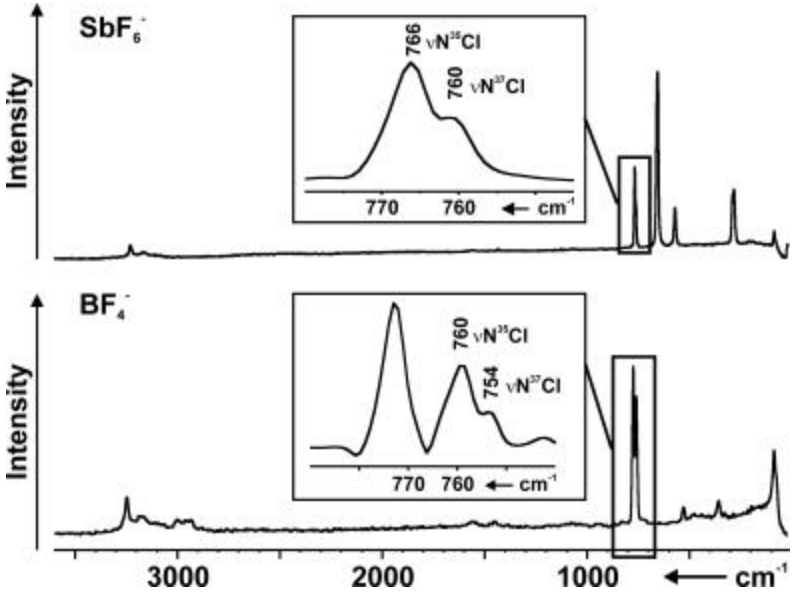

The NH_3Cl^+ Cation

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$NH_3Cl^+BF_4^-$, $NH_3Cl^+AsF_6^-$, and $NH_3Cl^+SbF_6$ are the first examples of stable salts containing a simple, inorganic cation with an N-Cl bond. They can be safely prepared from $(Me_3Si)_2NCl$ in mixtures of HF and the corresponding Lewis acids and could be used as storable gas generators for monochloramine.