is possible. Although measurements in D_2O become increasingly difficult as *n* increases because of solubility problems,[6] the advantages of making such measurements are considerable. Choice of an inert solvent is more important than choosing a solvent that minimizes the M $\leftarrow$ M and L $\leftarrow$ M band overlaps.

We note finally that, while more experimental work is needed, existing spectroscopic data in both D_2O and nitrobenzene support the initial prediction by Larsson[5] and the work of Launay et al.[6] of unusually slow falloff of coupling with distance for the complexes of the α,ω-dipyridyl *trans*-polyenes.

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Registry No. Decaammine[μ-[4,4′-(1,3-butadiene-1,4-diyl)bis[pyridine]-*N*:*N*′]]diruthenium(5+), 106219-83-4; decaammine[μ-[4,4′-(1,3,5-hexatriene-1,6-diyl)bis[pyridine]-*N*:*N*′]]diruthenium(5+), 118494-83-0; decaammine[μ-[4,4′-(1,3,5,7-octatetraene-1,8-diyl)bis[pyridinc]-*N*:*N*′]]diruthenium(5+), 118494-84-1.

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Evidence That the Cl_2F^+ Cation Has an Asymmetric Bent (C_s) Cl–Cl–F^+ Structure

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Equilibrium geometries, energies, infrared and Raman spectra, and bond strengths are theoretically predicted for symmetric Cl–F–Cl^+ (**1**) and asymmetric Cl–Cl–F^+ (**2**) by using quantum molecular structure theory. At the MP4(SDTQ)/6-311G-(2df)//MP3/6-311G(2df) + ZPE level, the asymmetric form **2** is calculated as 43.0 kcal/mol lower in energy than the symmetric isomer **1**. The predicted interatomic distances for **1** are 1.737 Å (Cl–F) and for **2** are 1.579 Å (Cl–F) and 1.953 Å (Cl–Cl). The C–F bond strength of **1** is calculated with D_0 = 21.2 kcal/mol. For **2**, dissociation energies are predicted as D_0(Cl–F) = 41.6 kcal/mol and D_0(Cl–Cl) = 63.3 kcal/mol. The theoretically computed vibrational frequencies and Raman intensities for the asymmetric isomer agree with those of the experimentally observed spectrum. The assignment of the IR spectrum to the symmetric form is incompatible with the theoretically predicted data. The bond strengths in both isomers are calculated by using isodesmic and isogyric reactions, and the results are compared with data for neutral and cationic Cl_2 and ClF.

Introduction

The preparation of the Cl_2F^+ cation in the form of its AsF_6^- and BF_4^- salts was first reported by Christe and Sawodny in 1969.[1] From the low-temperature infrared spectra, they concluded that the most probable structure for Cl_2F^+ is that of a symmetric, bent ion with C_{2v} symmetry.[1] Shortly afterward, Gillespie and Morton[2] published an analysis of the Raman spectra of the two salts and argued that the Cl_2F^+ cation has probably the asymmetric Cl–Cl–F^+ (C_s) structure. A subsequent theoretical investigation of the stabilities of the two forms of Cl_2F^+ by Joshi and Morokuma[3] supported the earlier suggestion of Christe and Sawodny[1] that Cl_2F^+ has a symmetric structure, because ab initio calculations at the 4-31G SCF level predicted that the symmetric C_{2v} form is lower in energy by ca. 10 kcal/mol than the asymmetric form. More recent calculations based on semiempirical[4] and higher level ab initio[5] methods gave an opposite stability sequence of the two isomeric forms. Because of the conflicting results, the latest edition of a modern textbook in chemistry came to the conclusion that, concerning the symmetric or asymmetric structure of Cl_2F^+, "...the question must be regarded as still open".[6]

We decided to provide a definitive answer to this question not only by performing high-level ab initio calculations on the structures and energies but also be calculating the infrared and Raman spectra of both forms of Cl_2F^+. We will show that the comparison of the theoretically predicted vibrational frequencies and IR and Raman intensities with the reported experimental values provides clear evidence that Cl_2F^+ has an asymmetric bent (C_s) Cl–Cl–F^+ structure.

Theoretical Details

All theoretical results have been obtained by using the CONVEX and IBM versions of the program series GAUSSIAN 86.[7] The geometries were first optimized at the Hartree–Fock (HF) and second-order Møller–Plesset (MP2) perturbation[8] levels by employing the 6-31G(d) basis set that includes a set of six d-type polarization functions.[9] These levels of theory are denoted by HF/6-31G(d) and MP2/6-31G(d), respectively. The harmonic vibrational frequencies and infrared intensities were computed at MP2/6-31G(d). Because Raman activities cannot be computed at the MP2/6-31G(d) level by GAUSSIAN 86, they have been calculated at the HF/6-31G(d) level. Since the computed results of the two isomers were found to be critically dependent on the size of the basis set used, we additionally optimized the geometries by employing the triply split valence basis set 6-311G augmented by two sets of five d-type functions and one set of seven f orbitals, i.e. 6-311G(2df).[10] Geometry optimizations were carried out at the HF, MP2, and MP3 levels by using 6-311G(2df). In order to predict energy differences more reliably, we calculated total energies with full fourth-order Møller–Plesset perturbation theory denoted as MP4//6-311G(2df), using the geometries obtained at MP3/6-311G(2df). The inner-shell orbitals were frozen in the calculations by using third- and fourth-order Møller–Plesset theory, but they have been included in the MP2 calculations. Thus, the highest level of theory employed in this paper is MP4/6-311G(2df)//MP3/6-311G(2df) + ZPE, with the ZPE corrections calculated at MP2//6-31G(d). Unless otherwise noted,

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Table I. Calculated Total Energies (E_{tot}, hartrees), Relative Energies (E_{rel}, kcal/mol), Zero-Point Vibrational Energies (ZPE, kcal/mol), Bond Lengths (r_{AB}, Å), and Bond Angles ($\angle_{ABC}$, deg) for $ClFCl^+$ (**1**) and $ClClF^+$ (**2**)

Cl–F–Cl$^+$ (**1**) ($^1A_1$)

	E_{tot}	E_{rel}	ZPE	r_{ClF}	$\angle_{ClFCl}$
HF/4-31G[a]	–1016.7509	0.0		1.80	140
HF/DZP[c]	–1017.8336	0.0		1.734	124.2
MP3/DZP[d]	–1018.3122	0.0			
HF/6-31G(d)	–1017.8234	0.0		1.736	122.8
MP2/6-31G(d)	–1018.2782	0.0	2.1	1.767	116.3
HF/6-311G(2df)	–1017.9094	0.0		1.721	123.1
MP2/6-311G(2df)	–1018.6558	0.0		1.745	116.0
MP3/6-311G(2df)	–1018.5393	0.0		1.737	118.6
MP4/6-311G(2df)[b]	–1018.5772	0.0			
MP*n*/6-311G(2df)[e]	–1018.5818	0.0			

Cl–Cl–F$^+$ (**2**) ($^1A'$)

	E_{tot}	E_{rel}	ZPE	r_{ClCl}	r_{ClF}	$\angle_{ClClF}$
HF/4-31G[a]	–1016.7358	9.5		2.270	1.704	99
HF/DZP[c]	–1017.8714	–23.7		1.989	1.565	102.3
MP3/DZP[d]	–1018.3617	–31.1				
HF/6-31G(d)	–1017.8562	–20.6		1.968	1.568	102.3
MP2/6-31G(d)	–1018.3210	–26.9	2.3	1.962	1.614	103.9
HF/6-311G(2df)	–1017.9699	–38.0		1.947	1.537	103.1
MP2/6-311G(2df)	–1018.7335	–48.8		1.924	1.584	104.7
MP3/6-311G(2df)	–1018.6120	–45.6		1.953	1.579	103.9
MP4/6-311G(2df)[b]	–1018.6460	–43.2				
MP*n*/6-311G(2df)[e]	–1018.6495	–42.5				

[a] Reference 3. [b] Geometries optimized at MP3/6-311G(2df). [c] Reference 5. [d] Reference 5; geometries optimized at HF/DZP. [e] Energy calculated by using eq 6.29 of ref 12 for an estimate of total correlation energy; see text.

energy values are given at this level of theory.

Results and Discussion

Table I shows the calculated energies and geometries of Cl_2F^+ in its symmetric form **1** and asymmetric form **2** at various levels of theory. At the Hartree–Fock level using the 4-31G basis set, **1** is more stable than **2** by 9.5 kcal/mol.[3] The opposite result is computed when a better basis set is employed. At HF/6-31(d), structure **2** is 20.6 kcal/mol lower in energy than **1**. A slightly larger value of 23.7 kcal/mol is predicted[5] with the DZ+P basis set.[11] With the even larger basis set 6-311G(2df), the energy difference increases to 38.0 kcal/mol in favor of **2**. It is known that polarization functions are necessary for a reliable description of molecules containing third-row elements.[12] A further extension of the basis set may yield an even higher energy difference. However, since the 6-311G(2df) basis set is fairly large, we do not expect a significantly different result with further extension of the basis set. Comparing the HF/4-31G results with the higher level data listed in Table I shows that the results are particularly different for the bond distances in **2**. The calculated Cl–F and Cl–Cl atomic distances are too long at HF/4-31G.

Inclusion of correlation energy using Møller–Plesset second-order perturbation theory increases the energy difference to 26.9 kcal/mol (MP2/6-31G(d)) and 48.8 kcal/mol (MP2/6-311G(2df)) in favor of **2**. This means that the quality of the basis set is more important for the computation of the energy difference between the two isomers of Cl_2F^+ than of the correlation energy. Higher order levels of perturbation theory slightly reduce the computed energy difference from 48.8 kcal/mol (MP2) to 45.6 kcal/mol (MP3) and 43.2 kcal/mol (MP4), using the 6-311G(2df) basis set (Table I). Correction by zero-point energies (Table I) gives a slightly smaller value of 43.0 kcal/mol. Thus, while the inclusion of correlation energy leads to an increase in the stability difference between **1** and **2**, this increase is reduced with higher level perturbation theory by 3.2 kcal/mol (MP2 → MP3) and 2.4 kcal/mol (MP3 → MP4). In order to estimate the contribution of still higher order levels, we used an empirical equation that has been suggested[18] for the calculation of total correlation energies E(corr):

$$E(\mathrm{corr}) = (E(2) + E(3))/(1 - E(4)/E(2))$$

The total energies calculated for **1** and **2** by using the estimated[13] total correlation energy E(corr) are also shown in Table I. The results predict that the effect of higher order contributions to the energy difference is very small; the estimated value corrected by ZPE is 42.3 kcal/mol. Taking the effects of the size of the basis set and the level of perturbation theory, we estimate that **2** should be 40–45 kcal/mol more stable than **1**.

That **2** is lower in energy than **1** has previously been calculated by using the semiempirical methods CNDO[4a,b] and MNDO[4c] and also by employing ab initio methods.[5] Although the higher stability is a strong indication that **2** rather than **1** is formed in the synthesis[1,2] of the salt compounds $Cl_2F^+AsF_6^-$ and $Cl_2F^+BF_4^-$, it is not impossible that the higher energy form **1** may actually be present in the solid. In order to gain further evidence that **2** is the experimentally observed species, we calculated the infrared

Table II. Experimentally Observed and Theoretically Predicted Vibrational Spectra for Cl_2^{+}[a]

Cl–F–Cl$^+$ (**1**)

	calc[e]		
exp[b] IR freq (int)	ν	IR int	Raman int
ν_1: 520 (vw),[c] 527 (mw),[c] 535 (m),[c] 519 (m),[d] 528 (mw),[d] 532 (mw, sh)[d]	577 (a_1)	5.8	11.7
ν_2: 258 (mw),[c] 293 (m)[c]	226 (a_1)	0.1	3.2
ν_3: 586 (mw),[c] 593 (m),[c] 588 (w, sh),[d] 594 (m)[d]	684 (b_2)	99.4	1.5

Cl–Cl–F$^+$ (**2**)

	calc[e]		
exp[f] Raman bands (rel int)	ν	IR int	Raman int
ν_1: 744 (78),[c] 743 (90)[d]	806 (a′)	44.8	17.9
ν_2: 528, 535 (100),[c] 516 (100),[d] 540 (90)	534 (a′)	13.3	18.7
ν_3: 293, 299 (20),[c] 296 (35)[d]	263 (a′)	6.9	4.1

[a] Frequencies are given in cm^{-1}, IR intensities in km/mol and Raman intensities in Å^4/amu. [b] Data and assignments are taken from ref 1. [c] $Cl_2F^+AsF_6^-$. [d] $Cl_2F^+BF_4^-$. [e] Frequencies and IR intensities are calculated at MP2/6-31G(d), and Raman intensities, at HF/6-31G(d). [f] Data and assignments are taken from ref 2.

Table III. Calculated (MP2/6-31G(d)) and Experimentally Observed[a] Vibrational Frequencies (ν, cm^{-1}) for Diatomics

molecule	ν(calc)	ν(exp)
ClF ($^1\Sigma^+_g$)	804	786
ClF^+ ($^2\Pi$)	1006	870,[b] 912[c]
Cl_2 ($^2\Pi_g$)	546	560
Cl_2^+ ($^1\Sigma^+_g$)	606	646

[a] Reference 20. [b] Reference 23. [c] Reference 24.

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Table IV. Calculated Total Energies (E_{tot}, hartrees), Zero-Point Vibrational Energies (ZPE, kcal/mol), Bond Lengths (r_{AB}, Å), and Eigenvalues of the S^2 Operator ($\langle S^2 \rangle$)

	HF/6-31G(d)		MP2/6-31G(d)			HF/6-311G(2df)	
	E_{tot}	r_{AB}	E_{tot}	r_{AB}	ZPE	E_{tot}	r_{AB}
ClF^+ ($^2\Pi$)	-558.3832	1.530	-558.6885	1.555	1.4	-558.4523	1.498
ClF ($^1\Sigma^+$)	-558.8195	1.613	-559.1268	1.659	1.1	-558.8834	1.592
Cl_2 ($^1\Sigma^+_g$)	-918.9128	1.990	-919.1714	2.015	0.8	-918.9789	1.982
Cl_2^+ ($^2\Pi_g$)	-918.5021	1.874	-918.7797	1.928	0.9	-918.5787	1.863
Cl (^{2}P)	-459.4480		-459.5524			-459.4759	
F (^{2}P)	-99.3650		-99.4890			-99.3987	

	MP2/6-311G(2df)		MP3/6-311G(2df)		MP4/6-311G(2df)	
	E_{tot}	r_{AB}	E_{tot}	r_{AB}	E_{tot}[a]	$\langle S^2 \rangle$
ClF^+ ($^2\Pi$)	-558.9408	1.527	-558.8696	1.526	-558.8949	0.76
ClF ($^1\Sigma^+$)	-559.4011	1.636	-559.3324	1.633	-559.3532	
Cl_2 ($^1\Sigma^+_g$)	-919.4736	1.991	-919.3816	2.009	-919.3974	
Cl_2^+ ($^2\Pi_g$)	-919.0540	1.901	-918.9601	1.907	-918.9785	0.77
Cl (^{2}P)	-459.6290		-459.6505		-459.6563	0.76
F (^{2}P)	-99.5932		-99.6041		-99.6079	0.76

[a] Using geometries optimized at MP3/6-311G(2df).

Table V. Theoretically Predicted Charge Distribution (MP4/6-311G(2df)) and Calculated[a] and Experimentally Observed[b] Equilibrium Distances (r_e, Å) and Dissociation Energies (D_0, kcal/mol)

structure	q(A)[c]	r_e(calc)	r_e(exp)	D_0(calc)	D_0(exp)
1	-0.19 (F) +0.60 (Cl)	1.737 (Cl-F)		21.2	
2	-0.12 (F) +0.83 (Cl_α) +0.29 (Cl_β)	1.579 (Cl-F) 1.953 (Cl-Cl)		41.6 (Cl-F) 63.3 (Cl-Cl)	
ClF ($^1\Sigma^+_g$)	+0.28 (Cl) -0.28 (F)	1.633	1.628	59.4	60.3
ClF^+ ($^2\Pi$)	+1.06 (Cl) -0.06 (F)	1.526	~1.526	68.4	67.5
Cl_2 ($^1\Sigma^+_g$)	0.0	2.009	1.988	58.0	57.1
Cl_2^+ ($^2\Pi_g$)	+0.5	1.907	1.892	90.1	91.0

[a] At MP4/6-311G(2df)//MP3/6-311G(2df) + ZPE using isodesmic reactions (see text). [b] Reference 20. [c] Partial charge at atom A. [d] Reference 23.

and Raman spectra of both isomers. The results are shown in Table II, together with the experimentally observed data and assignments as reported by Christe and Sawodny[1] and by Gillespie and Morton.[2]

The theoretically predicted frequencies may deviate substantially from experimental values due to basis set deficiencies, errors in the calculated correlation energy, and inaccuracies in the harmonic approximation. In many cases, the deviations are systematic and may be corrected by a scaling factor.[12,14] A systematic study of a large number of molecules showed that in most cases the vibrational frequencies are overestimated and that a scaling factor of 0.92 should be used at MP2/6-31G(d).[14] Some vibrational modes, however, are poorly described with this method, and the study does not include molecules with Cl-F and Cl-Cl bonds.[14] Table III shows our calculated vibrational frequencies for neutral and cationic Cl_2 and ClF in comparison with experimentally derived data. The theoretically predicted Cl-F stretching modes are too high by 2.2% (ClF) and 10.3-15.6% (ClF^+). In contrast, the calculated Cl-Cl frequencies are too low by 2.9% (Cl_2^+) and 6.2% (Cl_2). The results shown in Table III will be used to estimate the accuracy of our computed vibrational spectra for **1** and **2**.

The data in Table II show that the calculated frequency for the Cl-F stretching mode ν_1 of the asymmetric isomer **2** is too high by 62 or 63 cm^{-1} (7.7%). This is intermediate to what has been calculated for the frequencies of ClF (2.2%) and ClF^+ (10.3-15.6%), which are also too high (Table III). Since the Cl-F interatomic distance in **2** is also intermediate between the bond lengths calculated for ClF and ClF^+ (Table V), we estimate that ν_1 of **2** should be corrected by 40-80 cm^{-1}, which brings the calculated value into the range of the observed frequency.

Two bands at 516 and 540 cm^{-1} are observed for the Cl-Cl stretching mode ν_2 of $Cl_2F^+BF_4^-$, which is probably due to factor group splitting.[2] The splitting for ν_2 of $Cl_2F^+AsF_6^-$ is much smaller at 528 and 535 cm^{-1} (Table II). The calculated frequency for ν_2 (534 cm^{-1}) matches the experimental values very closely. The data in Table III show that the calculated Cl-Cl frequencies are too low by 14 cm^{-1} (Cl_2^+) and 40 cm^{-1} (Cl_2). These data suggest a correction by 20-30 cm^{-1} for ν_2 to a higher value, which makes the calculated frequency slightly too large. The theoretically predicted bending mode ν_3 is ~30 cm^{-1} too low (Table II). Because no empirical scaling factor is available, we did not try to correct this value. Thus, the computed vibrational frequencies for structure **2** agree within ~30 cm^{-1} with the experimental values reported by Gillespie and Morton.[2]

More important than the frequencies are the Raman intensities. Table II shows that the theoretically computed Raman activities for **2** (ν_1 17.9 Å^4/amu, ν_2 18.7 Å^4/amu, ν_3 4.1 Å^4/amu) predict exactly the relative intensities of the three Raman bands that are actually found by experiment. This agreement is a very strong indication that the assignment of the Raman spectra of the two salts to the fundamentals of asymmetric Cl_2F^+ by Gillespie and Morton[2] is correct.

The comparison of the computed frequencies for **1** with the assigned infrared signals by Christe and Sawodny[1] shows a larger deviation for ν_2, if the experimental value of 293 cm^{-1} is taken as reference, which is probably correct. For reasons mentioned above, this deviation is not sufficient to suspect a wrong assignment. The agreement between theoretically predicted and experimentally reported frequencies for ν_1 and ν_3 is satisfactory. The calculated symmetric and asymmetric Cl-F stretching modes are too high by about 50 and 100 cm^{-1}, respectively, which is in accord with the overestimation of the Cl-F stretch in ClF and ClF^+ (Table III).

The most important result of the computed infrared spectrum of **1** is the fact that the predicted IR intensity is inconsistent with the assignment made by Christe and Sawodny.[1] The interpretation of the experimentally obtained IR spectrum assigns three bands of medium or medium weak intensity to the three fundamentals of **1**. The calculated results show that the IR spectrum of 1 should exhibit a weak band for ν_1 and a very strong band for ν_3, while ν_2 should hardly be visible. This is in sharp contrast to the assignment of the infrared spectrum for $Cl_2F^+BF_4^-$ and $Cl_2F^+AsF_6^-$ as reported by Christe and Sawodny. In particular, the relative intensities of ν_2 and ν_3 are incompatible with the computed IR intensities shown in Table II. The weak to medium weak band at 586–594 cm^{-1}, which was assigned to the asymmetric Cl–F stretching mode by Christe and Sawodny, appears to be rather the overtone of the bending mode observed at 293–299 cm^{-1} by Gillespie and Morton.[2]

The theoretically predicted IR spectrum for **2** shows good agreement for ν_2 and ν_3 with the reported IR data of Christe and Sawodny that were assigned to structure **1**.[1] However, there remains a discrepancy between theory and experiment concerning ν_1. As it was discussed above, the fundamental mode ν_1 should be observed in the range 720–760 cm^{-1} with a strong intensity in the Raman *and* the IR spectrum. While the experimentally observed Raman spectrum exhibits this mode very clearly[2] at 743 cm^{-1} ($CL_2F^+BF_4^-$) and 744 cm^{-1} ($Cl_2F^+AsF_6^-$), the corresponding IR band is only observed for Cl_2FAsF_6 at 703 cm^{-1}.[1] ν_1 corresponds to the Cl–F stretching mode, and the change in the dipole moment of **2** resulting from Cl–F stretching should be significant. There are two questions. First, why is the high-intensity mode ν_1 for $Cl_2F^+AsF_6^-$ observed at 744 cm^{-1} in the Raman spectrum[2] shifted by 41 cm^{-1} when the IR spectrum is recorded?[1] Second, why is this mode missing in the IR spectrum of $Cl_2F^+BF_4^-$? A reinvestigation of the IR spectrum of $Cl_2F^+BF_4^-$ and $Cl_2F^+AsF_6^-$, perhaps in solution rather than in the crystal form, would help to answer these questions.

In order to gain insight into the strength of the binding interactions in the two isomers of Cl_2F^+, we calculated the dissociation energies D_0 for the energetically lowest lying fragmentation reactions of **1** and **2**. Cl_2F^+ has previously been discussed[3,15] as the product of ClF and Cl^+, because ClF + AsF_5 (or BF_3) is used for the synthesis of the salt compounds.[1] A qualitative discussion based on frontier orbital theory[16] came to the conclusion that frontier orbital interactions between the LUMO of Cl^+ and the HOMO of ClF should yield the asymmetric form.[15] The energy decomposition analysis of the interaction energy between Cl^+ and ClF, which was computed as 57.1 kcal/mol for **1** and 47.6 kcal/mol for **2**, suggests that charge-transfer and polarization terms are responsible for the stability of **1**.[3] However, the energetically lowest lying fragmentation process of **1** and **2** is the loss of a neutral chlorine atom. This is because the ionization energy of ClF (12.66 eV)[17] is *lower* than that of Cl (12.97 eV).[17]

Table IV shows the computed energies of some fragments of **1** and **2**. It is gratifying that the eigenvalues of the S^2 operator, $\langle S^2 \rangle$, are close to the value for a pure doublet state (0.75), which indicates that spin contamination is very low. We will begin our discussion with the calculated reaction energies of **1**. The Cl–F bond strength of **1** may be estimated by calculating ΔE_0 of reaction 1 (all energies are calculated at the MP4/6-311G(2df)//MP3/6-311G(2df) + ZPE(MP2/6-31G(d)) level).

$$Cl_2F^+\ (\mathbf{1}) \rightarrow ClF^+\ (^2\Pi) + Cl\ (^2P) \qquad +15.6\ \text{kcal/mol} \qquad (1)$$

The calculated value of ΔE_0 = 15.6 kcal/mol may not be very accurate, because reaction 1 is not isogyric;[18] i.e. the numbers of unpaired electrons on the left and right sides of the reaction are not the same. A more reliable way to compute dissociation energies is given by using isogyric and isodesmic[19] reactions such as (2), where the number of unpaired electrons and the types of bonds are conserved.

$$Cl_2F^+\ (\mathbf{1}) + F\ (^2P) \rightarrow ClF^+\ (^2\Pi) + ClF\ (^1\Sigma^+_g) \qquad -39.1\ \text{kcal/mol} \qquad (2)$$

Combination of the calculated energy for reaction 2, ΔE_0 = −39.1 kcal/mol, and the experimentally observed dissociation energy of ClF ($^1\Sigma^+_g$), D_0 = 60.3 kcal/mol,[20] gives a theoretically predicted Cl–F bond energy of 21.2 kcal/mol for **1**.

The Cl–F and Cl–Cl bond strength in structures **2** may first be estimated by calculating the reaction energies for reactions 3 and 4.

$$Cl_2F^+\ (\mathbf{2}) \rightarrow Cl_2^+\ (^2\Pi_g) + F\ (^2P) \qquad +36.0\ \text{kcal/mol} \qquad (3)$$

$$Cl_2F^+\ (\mathbf{2}) \rightarrow ClF^+\ (^2\Pi) + Cl\ (^2P) \qquad +58.6\ \text{kcal/mol} \qquad (4)$$

More accurate data for the bond strengths are provided via the isogyric and isodesmic reactions (5) and (6).

$$Cl_2F^+\ (\mathbf{2}) + Cl\ (^2P) \rightarrow Cl_2^+\ (^2\Pi_g) + ClF(^1\Sigma^+_g) \qquad -18.7\ \text{kcal/mol} \qquad (5)$$

$$Cl_2F^+\ (\mathbf{2}) + Cl\ (^2P) \rightarrow ClF^+\ (^2\Pi) + Cl_2\ (^1\Sigma^+_g) \qquad +6.2\ \text{kcal/mol} \qquad (6)$$

The combination of the calculated reaction energy (ΔE_0 = −18.7 kcal/mol) for reaction 5 and the observed bond strength of ClF (D_0 - 60.3 kcal/mol)[20] gives a theoretically predicted Cl–F bond strength of 41.6 kcal/mol for **2**. From the reaction energy (ΔE_0 = +6.2 kcal/mol) for reaction 6 and the dissociation energy of Cl_2 (D_0 = 57.1 kcal/mol)[20] a bond energy of 63.3 kcal/mol is predicted for the Cl–Cl bond in **2**.

The bond strengths in **1** and **2** may be compared with the corresponding D_0 values for neutral and cationic ClF and Cl_2, respectively. Table V shows the experimentally observed[20] D_0 data and the theoretically predicted results that are obtained by using the isogyric reactions (7) and (8).

$$Cl_2\ (^1\Sigma^+_g) + F\ (^2P) \rightarrow ClF\ (^1\Sigma^+_g) + Cl\ (^2P) \qquad -2.3\ \text{kcal/mol} \qquad (7)$$

$$Cl_2^+\ (^2\Pi_g) + F\ (^2P) \rightarrow ClF^+\ (^2\Pi) + Cl\ (^2P) \qquad +22.6\ \text{kcal/mol} \qquad (8)$$

The calculated dissociation energies D_0 for the diatomic species deviate in all cases by only ~1.0 kcal/mol from the experimental values (Table V). Because of the very good agreement, we expect the D_0 values for **1** and **2** to be correct within ±3 kcal/mol. The calculated equilibrium distances for the four diatomic molecules show a maximum deviation of 0.02 Å with a tendency toward longer bonds. The computed interatomic distances in **1** and **2** may therefore also be slightly too long.

The Cl–F bond in **1** is very weak (21.2 kcal/mol), while it is twice as strong in **2** (41.6 kcal/mol). Yet, the Cl–F bond in **2** is still weaker than in neutral ClF (59.4 kcal/mol) or cationic ClF^+ (68.4 kcal/mol). The Cl–Cl bond in **2** is stronger (63.3 kcal/mol) than the Cl–F bond. It is also slightly stronger than the Cl–Cl bond in Cl_2 (58.0 kcal/mol), but significantly weaker than the Cl–Cl bond in Cl_2^+ (90.1 kcal/mol).[21] The charge distribution calculated by the Mulliken population analysis[22] predicts a negatively charged fluorine atom in **1** and **2**. Thus, the chlorine atoms carry all of the positive charge.

Summary

The total energies calculated at the MP4(SDTQ)/6-311G(2df) level by using geometries obtained at MP3/6-311G(2df) and corrected by zero-point vibrational energies show that asymmetric $Cl–Cl–F^+$ (**2**) is 43.0 kcal/mol more stable than the symmetric form $Cl–F–Cl^+$ (**1**). The theoretically predicted vibrational fre-

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[21] As shown in Table V, the bond strength in neutral ClF is slightly higher than that in neutral Cl_2, while Cl_2^+ is much more strongly bound than ClF^+. This can be explained as follows. Ionization of Cl_2 and ClF removes an electron from a π^* antibonding orbital, which yields stronger bonds in both cases (Table V). This effect is much stronger for Cl_2, because the π^* orbital in Cl_2 is symmetric, while in ClF the π^* HOMO is located mainly at the chlorine atom with little antibonding character.

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quencies and Raman intensities agree well with the experimentally obtained data and assignments for **2** reported by Gillespie and Morton.[2] The experimental infrared spectrum of Cl_2F^+, which was assigned to the symmetric form by Christe and Sawodny,[1] is incompatible with the calculated IR spectrum for **1**. The Cl–F bond strength in **2** is predicted as 41.6 kcal/mol, significantly higher than in **1** (21.2 kcal/mol) but lower than in diatomic ClF (59.4 kcal/mol) and ClF^+ (68.4 kcal/mol). The Cl–Cl bond in **2** is quite strong (63.3 kcal/mol), even stronger than in Cl_2 (58.0 kcal/mol) but weaker than in Cl_2^+ (90.1 kcal/mol).

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Formation of Amine, Phosphine, and Thioether Adducts of Chlorotriborane(7)

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The chlorotriborane(7) (B_3H_6Cl) adduct of $N(CH_3)_3$ was formed by the reaction of $B_4H_8{\cdot}N(CH_3)_3$ with HCl in dichloromethane or with $HgCl_2$ in chloroform. The reaction of $B_3H_7{\cdot}N(CH_3)_3$ with BCl_3 in dichloromethane was found to be a better preparative method for $B_3H_6Cl{\cdot}N(CH_3)_3$. The BCl_3 treatment was employed to convert the $N(CH_3)_2H$, $N(CH_3)H_2$, NH_3, and $S(CH_3)_2$ adducts of B_3H_7 into the corresponding adducts of B_3H_6Cl. In contrast, $B_3H_7{\cdot}P(CH_3)_3$ and $B_3H_7{\cdot}PH_3$ are inert to BCl_3. The B_3H_6Cl adducts of $P(CH_3)_3$ and PH_3 could be obtained by treating the B_3H_7 adducts with a mixture of HCl and BCl_3 in dichloromethane. The ^{11}B and ^1H NMR spectra of these B_3H_6Cl adducts showed that their structures were described as 1-(Lewis base)-2-chlorotriborane(7).

Introduction

In an earlier report from this laboratory, the formation of trimethylamine–chlorotriborane(7) was mentioned briefly.[1] The compound was formed when $B_4H_8{\cdot}N(CH_3)_3$ was treated with hydrogen chloride in dichloromethane. In literature prior to that time, the $B_3H_7Cl^-$ and $B_3H_7Br^-$ anions were the only halogenated derivatives of B_3H_7 adducts that were reported.[2] Subsequently, preparative studies of the neutral chlorotriborane adducts were pursued.[3]

In recent years, Morris and co-workers developed the chemistry of the above halogenated triborohydride anions and reported several new triborohyride anions, including pseudohalogen derivatives.[4] The reaction chemistry of the $B_3H_8^-$ derivatives is of interest, since a variety of new borane derivatives are expected to be synthesized from these compounds. The corresponding derivatives of the neutral B_3H_7 adducts are throught to have different reactivities due to the absence of the negative charge, and they too may serve as the starting compounds for the syntheses of new boron hydride compounds. In this paper, the results of our preparative studies of chlorotriborane(7) adducts are described.

Results

(A) Trimethylamine–Chlorotriborane(7). (a) Formation of $B_3H_6Cl{\cdot}N(CH_3)_3$. Trimethylamine–chlorotriborane(7) was formed in the rections given in eqs 1–4. The reaction of $B_4H_8{\cdot}N(CH_3)_3$

$$B_4H_8{\cdot}N(CH_3)_3 + HCl \xrightarrow[\text{in } CH_2Cl_2]{} B_3H_6Cl{\cdot}N(CH_3)_3 + {}^1\!/\!_2B_2H_6{}^{1a} \quad (1)$$

$$B_3H_7{\cdot}N(CH_3)_3 + BCl_3 \xrightarrow[\text{in } CH_2Cl_2]{} B_3H_6Cl{\cdot}N(CH_3)_3 + \text{“}BHCl_2\text{”} \quad (2)$$

$$B_3H_7{\cdot}N(CH_3)_3 + HCl \xrightarrow[\text{in } CH_2Cl_2]{BCl_3} B_3H_6Cl{\cdot}N(CH_3)_3 + H_2 \quad (3)$$

$$B_4H_8{\cdot}N(CH_3)_3 + 2HgCl_2 \xrightarrow[\text{in } CHCl_3]{} B_3H_6Cl{\cdot}N(CH_3)_3 + Hg_2Cl_2 + \text{“}H_2BCl\text{”} \quad (4)$$

with HCl was accompanied by another reaction (eq 5) that yielded

$$B_4H_8{\cdot}N(CH_3)_3 + HCl \xrightarrow[\text{in } CH_2Cl_2]{} B_3H_7{\cdot}N(CH_3)_3 + \text{“}BH_2Cl\text{”} \quad (5)$$

$B_3H_7{\cdot}N(CH_3)_3$.[1a] Thus, a mixture of $B_3H_7{\cdot}N(CH_3)_3$ and $B_3H_6Cl{\cdot}N(CH_3)_3$ (ca. 3:7 molar ratio) was obtained. Hydrogen bromide reacted with $B_4H_8{\cdot}N(CH_3)_3$ in a manner similar to the HCl reaction (eqs 1 and 5), and $B_3H_6Br{\cdot}N(CH_3)_3$ and $B_3H_7{\cdot}N(CH_3)_3$ were produced.

The reaction expressed in eq 2 is currently the best method for the preparation of $B_3H_6Cl{\cdot}N(CH_3)_3$. The reaction proceeded to near completion at −80 °C. Performing the reaction at higher temperatures (−40 to −23 °C) with excess BCl_3 ensured the complete conversion of $B_3H_7{\cdot}N(CH_3)_3$ to $B_3H_6Cl{\cdot}N(CH_3)_3$. Equation 3 could also be used for the $B_3H_6Cl{\cdot}N(CH_3)_3$ preparation; the reaction was completed at −80 °C within a short period of time. The chlorotriborane(7) adduct was also formed in the slow reaction of $B_3H_7{\cdot}N(CH_3)_3$ with hydrogen chloride, in the absence of BCl_3, in CH_2Cl_2 at room temperature. However, many other boron hydride compounds were formed as the side products. In tetrahydrofuran, $B_3H_7{\cdot}N(CH_3)_3$ was practically inert to HCl.[5]

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