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Contribution from the Department of Theoretical Chemistry,
University of Sydney, NSW 2006, Australia

Electron Transfer and Energy Transfer through Bridged Systems. 5. Intermetallic Coupling and Electronic Spectra of the Bis(pentaammineruthenium) Complexes of α,ω-Dipyridyl *trans*-Polyenes in Nitrobenzene

J. R. Reimers and N. S. Hush*

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A theoretical model is developed to predict the electronic coupling between the metal centers within the bis(pentaammineruthenium) complexes of the α,ω-dipyridyl polyenes of length $n = 2$–4 in nitrobenzene solution. This model is parametrized by extrapolation of the parameters deduced earlier for the $n = 0$–2 complexes in D_2O solution. The results predict much smaller couplings than those reported by Woitellier, Launay, and Spangler, and a large part of this difference is removed by a detailed reanalysis of their raw experimental spectral data. Deconvolution of the overlapping metal to ligand and intervalence bands is performed, improved comproportionation constants are used, and corrections for the nonplanarity of the ligands are introduced.

Introduction

The bis(pentaammineruthenium) complexes of α,ω-dipyridyl *trans*-polyenes (Figure 1) form a series of semirigid molecules in which the metal–metal separation increases almost linearly with polyene length n. As predicted by Hush[1,2] and first observed by Tom, Creutz, and Taube,[3,4] the mixed-valence Ru^{II}–Ru^{III} ions display an intervalence transition whose intensity is related to the electronic coupling between the metal d_π orbitals. Because of the large intermetallic separation, this coupling is not due to any direct through-space overlap of the d_π orbitals but rather is due principally to a through-bridge-mediated interaction. The $M \leftarrow M$ transition is a specific example of an electron-transfer process, occurring here over large distances under somewhat controlled conditions. Larsson[5] has predicted that the α,ω-dipyridyl *trans*-polyene ligands should give rise to a very slow falloff of coupling with distance, and this conclusion has been verified by Woitellier, Launay, and Spangler.[6] This property renders these ligands of interest as possible components of molecular electronic devices.

For the $n = 0$ and $n = 1$ complexes in D_2O, the intermetallic coupling is known to be 390 and 300 cm^{-1}, respectively.[7,8] Recently, Woitellier, Launay, and Spangler[6] synthesized the $n = 2$–4 complexes as part of an ongoing research program into the basics of molecular switch[9] design. They observed the intervalence spectra of all three complexes in nitrobenzene, from which they deduced intermetallic couplings of 340, 260, and 240 cm^{-1} for $n = 2$–4, respectively. Also, they reported spectra for the $n = 2$ complex in D_2O, and we[8] analyzed these spectra and concluded that the intermetallic coupling is 260 ± 50 cm^{-1}. At first sight, the results in D_2O appear inconsistent with the results in nitrobenzene; rationalization of these two sets of data is the purpose of this work.

First, we perform a reanalysis of the overlapping $M \leftarrow M$ and $M \leftarrow L$ bands reported by Woitellier, Launay, and Spangler.[6] These numbers are then corrected for comproportionation and for nonplanarity of the ligands.

Second, we construct a theoretical model to describe the coupling as a function of both solvent and bridge length. Hückel methods are often employed for modeling electronic interactions in inorganic complexes; they are inappropriate here because they contain too many empirical parameters and can easily be adapted to reproduce any desired bridge-length dependence. The model used here is described in detail in the previous paper in this series.[8] Briefly, it employs a CNDO/S[10] calculation to generate molecular orbitals for the ligand, and these orbitals are then combined in an empirical tight-binding calculation with ruthenium d_π orbitals to form a description of the electronic interactions in the bis(ruthenium) complexes. One empirical parameter β_{M-N} is introduced to describe the nitrogen–d_π coupling in all valence states of all complexes in all solvents, and three (solvent-dependent) parameters per ligand are introduced and determined from a knowledge of the intervalence band frequency and the lowest lying metal to ligand and ligand to metal frequencies. Thus, this model contains no parameters that are adjusted in order to fit observed coupling constants, and therefore it can be considered as a predictive technique rather than an interpretive technique. It is known[8] to predict accurately the intermetallic couplings seen in D_2O solution; here it is applied in order to understand the observed couplings in nitrobenzene solution.

Table I. Parameters Used for Each Ligand

			energy gap/eV		
ligand	r_{MM}/Å	K_c	$\Delta E_{III,II}$	$\Delta E_{L,II}$	$\Delta E_{III,H}$
$n = 2$	15.7	14.0	1.17	2.27	3.02
$n = 3$	18.0	11.9	1.12	2.27	2.72
$n = 4$	20.3	10.5	1.20	2.27	2.50

Analysis of Experimental Data

Woitellier, Launay, and Spangler[6] reported the intervalence bands for the $n = 2$–4 complexes in nitrobenzene, but because of the equilibrium

$$Ru^{II}\text{–}Ru^{II} + Ru^{III}\text{–}Ru^{III} \overset{K_c}{\rightleftharpoons} 2Ru^{II}\text{–}Ru^{III} \qquad (1)$$

their measurements of the observed intervalence $M \leftarrow M$ absorption intensities must be corrected to indicate the true concentration of dimer. Ideally, the comproportionation constant K_c should be measured experimentally, but this is a difficult task for small $K_c < 15$ and thus K_c has to date not been measured. We showed[8] that, to a good approximation, K_c in aqueous solution is given from an electrostatic model as

$$K_c = 4 \exp\left(\frac{1}{\epsilon r_{MM} k T}\right) \qquad (2)$$

where the parameter ϵ is the dielectric constant of the material between the metal atoms separated a distance r_{MM} (the "material" in this case consists of both ligand and solvent, but as the respective dielectric constants are similar, one expects that this formula will remain a good approximation). Sutton and Taube[7] observed that $K_c = 23$ for the $n = 0$ ligand in ethylene glycol, and because of the similarity in the dielectric constants, we expect that this value is also appropriate in nitrobenzene. The value of the parameter ϵ is thus determined, and from values for the intermetallic spacing r_{MM} given in Table I (these values are estimated by using a geometric model[8]), K_c is estimated for $n = 2$–4 in nitrobenzene

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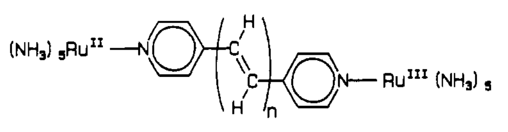

Figure 1. *trans*-Bis(*p*-pentaammineruthenium) complexes of α,β-dipyridyl polyenes with polyene length *n*.

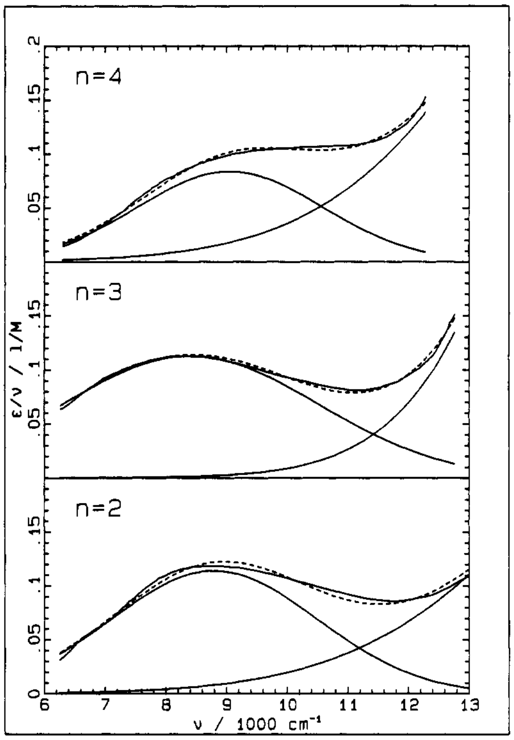

Figure 2. Observed[6] intervalence spectra and the deconvoluted Gaussian bands. The dashed curves are the sums of the deconvoluted bands.

Table II. Properties of the Intervalence Bands

ligand	ν_m/cm^{-1}	Δ/cm^{-1}	$(\epsilon/\nu)_m$/M^{-1}	μ/e Å
$n = 2$	8800	3930	0.114	0.45
$n = 3$	8410	4810	0.113	0.50
$n = 4$	9060	3540	0.084	0.37

and the results are given in Table I. If we assume that the homovalent II–II and III–III species do not absorb in the intervalence region, then correction of Woitellier, Launay, and Spanger's observed data for comproportionation reduces to a simple rescaling of the spectra; the rescaled intervalence M ← M spectra are given in Figure 2 for n = 2–4.

Interpretation of the M ← M spectra is not simple because of the overlap seen between the M ← M band and the tail of the intense L ← M band. The central limit theorem of statistics suggests that the scaled extinction coefficient ϵ/ν should be a Gaussian function of the absorption frequency ν, and thus we fit Gaussian band shapes to the observed M ← M bands and to the tail of the observed L ← M bands. These Gaussian bands are also given in Figure 2, and the sum of these bands is given as a dashed curve. Excellent agreement is seen for the fits of the M ← M bands of the n = 3 and 4 complexes, and the fit for the n = 2 complex is adequate. In Table II are given the resulting band maxima ν_m, absorption peaks $(\epsilon/\nu)_m$, and peak full widths at half-maximum Δ. There, also is given the effective intermetallic coupling matrix element defined[1,8] via

$$\bar{V}_{12} = \mu\nu/r_{MM} \qquad (3)$$

where μ is the transition moment in units of e Å and r_{MM} is in units of Å.

Table III. Calculated and Observed (Both Raw Data and Planarity Corrected Data) Effective Intermetallic Coupling Constants $\bar{V}_{12}$[a]

		$\bar{V}_{12}$/cm^{-1}			
		WLS	obsd		
solvent	ligand	raw	raw	corr	calcd
D_2O	$n = 0$		390	460	476
D_2O	$n = 1$		300	330	364
D_2O	$n = 2$		260[b]	285[b]	253
nitrobenzene	$n = 2$	340	255	280	209
nitrobenzene	$n = 3$	260	235	260	138
nitrobenzene	$n = 4$	249	165	180	103

[a] The original observed raw nitrobenzene couplings deduced by Woitellier, Launay, and Spangler (WLS) are also given, as is data for D_2O taken from ref 8. [b] Approximate only, ±50 cm^{-1}.

Another difficulty in the interpretation of the experimental data arises as the dipyridyl polyene ligands are not held rigidly in planar configurations, but rather large-amplitude torsional displacements occur. In order to facilitate discussions of the general form of the bridge-length dependence of electron-transfer rates, it is necessary to correct the experimental data for this effect, which is specific to dipyridyl polyene systems. From both theoretical[8,11] and experimental[8] grounds, one expects that the effective intermetallic coupling decreases as the product of the cosines of each of the internal torsional angles. From data for styrene,[12] we estimate[8] that the thermally averaged weighted ring–double-bond torsional angle is 17°, and planarity corrected values for the observed couplings are given in Table III. Note that we do not include corrections for any of the double-bond–double-bond torsional angles, but these corrections could be significant for the longer chains even if the thermally averaged torsional angle is as little as 10°. Such additional corrections would increase the planarity corrected couplings at large *n*.

Theoretical Model

So as to understand the trends seen in the observed planarity corrected coupling constants, theoretical values for the intermetallic coupling are deduced and are given in Table III. They are obtained by calculation of the transition moment by using the model of ref 8 and thence the coupling by using eq 3. First, CNDO/S calculations are performed to determine the molecular orbitals of the free ligands, and the orbital basis is then fortified to include two metal d_π orbitals that are coupled only to the nitrogen atom's π orbitals. Four parameters are thus introduced: the energy gap $\Delta E_{III,II}$ between the two metal d_π orbitals, the energy gap $\Delta E_{L,II}$ between the Ru^{II} d_π orbital and the ligand LUMO orbital, the energy gap $\Delta E_{III,H}$ between the Ru^{III} d_π orbital and the ligand HOMO orbital, and the metal to nitrogen coupling $\beta_{M\text{-}N}$. Note that three energy gaps are required for each ligand (in each solvent), while $\beta_{M\text{-}N}$ is common to all ligands and solvents. We use $\beta_{M\text{-}N} = -0.95$ eV, consistent with the analysis of the n = 0–2 complexes and the pyridyl complex in D_2O, and use values of $\Delta E_{III,II}$ adjusted to fit the intervalence spectral maxima. These values are given in the parameter table, Table I.

Values of $\Delta E_{L,II}$ and $\Delta E_{III,H}$ should, in principle, be extracted from the L ← M and M ← L spectra, respectively, but these spectra are not available for the n = 2–4 ligands in nitrobenzene. Indeed, transitions within nitrobenzene itself make observation of these bands difficult, as also does transitions in the Fe(2,2′-bipyridine)$_3$ complex commonly used as oxidant. From the available information,[6] it appears that the L ← M band shifts very little over $0 \le n \le 2$ in D_2O and $2 \le n \le 4$ in nitrobenzene. This enables an estimate for $\Delta E_{L,II}$ to be made, but it is more difficult to estimate $\Delta E_{III,H}$, as little information is available concerning the M ← L transitions. For n = 2, we use for $\Delta E_{III,H}$ the values observed in D_2O solution, and for the n = 3 and n = 4 ligands, we note that CNDO/S is quite accurate[8] in predicting changes in the M ← L energy over $0 \le n \le 2$ in D_2O, and thus we use CNDO/S to estimate values for $\Delta E_{III,H}$. Specifically, we equate the difference in the M ← L band frequencies to differences in $\Delta E_{III,H}$, which are equated to differences in the CNDO/S ligand HOMO orbital energies, and thus the values of $\Delta E_{III,H}$ for n =

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3 and $n = 4$ are extrapolated from the value for $n = 2$.

Discussion and Conclusions

The most significant problem anticipated with the interpretations presented in Figure 2 is with the interpretation of the $n = 2$ spectrum. While the other spectra are easily fitted as a Gaussian band plus a Gaussian tail, the spectrum of $n = 2$ is not. Intuitively, one feels that the Gaussian tail should fall off faster than the fit indicates, and thus the deduced coupling constant could be too small by as much as 15%.

The couplings observed and calculated for the $n = 0$, 1, and 2 ligands in D_2O[7,8] are given in Table III for comparison with the data for the $n = 2$–4 ligands in nitrobenzene. One might suspect from the original raw nitrobenzene couplings reported by Woitellier, Launay, and Spangler[6] that the coupling is considerably enhanced in nitrobenzene as compared to D_2O. However, the raw couplings deduced herein for nitrobenzene are considerably lower than the couplings originally reported, and the nitrobenzene results no longer seem inconsistent with the D_2O results.

While some of the differences between the original and the revised couplings in nitrobenzene are due to the use of a new estimate for K_c, most of the differences are due to the use of deconvolution techniques. To some extent, these differences are also a measure of the inherent difficulties involved in deconvoluting spectra, especially when only a small part of a major band is known. In situations such as this, it is important to measure the whole of the interfering L ← M band so that a reasonable estimate of its band contour can be made; e.g., see the analysis[8] of the spectra of Taube et al. for $n = 0$ and 1 in D_2O.

Very good agreement is seen between the theoretical and observed planarity corrected couplings in D_2O,[8] and there is qualitative agreement between the coupling falloffs over the range $n = 2$–4 in nitrobenzene. The major difference between the two sets of couplings is that the theoretical calculations predict that the coupling should be weaker in nitrobenzene than in D_2O whereas the revised experimental results indicate that the coupling is similar in both solvents. Certainly, the theoretical calculations, which are predictive in nature rather than interpretive, verify the physical interpretation of the spectra and verify the original[5,6] prediction of a very weak dependence of the coupling on bridge length.

Several sources of potential problems with the theoretical model exist, and these could give rise to the observed differences between theory and experiment. The model does not take configuration interaction specifically into account, and it does not include the inductive effects arising from the presence of nearby charges on the nature of the ligand orbitals. Also, the model slightly misrepresents the energy of the $\pi^* \leftarrow \pi$ states.[8] We are investigating ways of improving these aspects, including use of the Hartree–Fock–Slater discrete variational ($X\alpha$) technique,[13] use of an INDO method parametrized for the second transition series,[14,15] and use of effective potential techniques.[16] More important problems also arise because the implementation of the model herein relies on the calculation of the parameters $\Delta E_{\mathrm{L,II}}$ and $\Delta E_{\mathrm{III,H}}$ via estimation of the lowest L ← M and M ← L transition energies in nitrobenzene. If either of these transition energies is lower than the estimated values used here as data, then the calculated coupling constants could increase significantly (e.g., for $n = 3$ if the M ← L frequency is decreased to 20 000 cm^{-1}, then the calculated coupling increases to 210 cm^{-1}); indeed, the effect increases as n increases due to the larger range over which the parameters are extrapolated. It is of considerable assistance to this theoretical model if UV/vis spectra of the homovalent II–II and III–III species could be obtained in nitrobenzene or some similar but transparent solvent (e.g. benzonitrile).

Analysis of a *preliminary* spectrum[17] of the $n = 2$ complex in nitromethane ($\nu_m = 9150$ cm^{-1}, $\Delta = 5000$ cm^{-1}, and $(\epsilon/\nu)_m = 0.041$ M^{-1} by using estimated $K_c = 14.0$, $\mu = 0.31$ e Å, and raw $\bar{V}_{12} = 180$ cm^{-1}) gives a planarity corrected coupling of 195 cm^{-1}, close to the theoretical value of 217 cm^{-1} for this solvent. This suggests that the theory is reliable. It would be helpful if a definitive determination of the intervalence spectrum of at least the $n = 2$ complex in nitromethane is obtained.

Problems still exist with the interpretation of the experimental data also. For example, no simple interpretation exists for the nonmonotonic changes observed in the widths and locations of the M ← M bands; see Table II. In D_2O, spectral changes with increasing bridge length follow a smooth, interpretable pattern, and thus this observation also suggests that additional physical effects contribute to the nitrobenzene spectra. CNDO/S calculations[8] predict that the lowest M ← L transition becomes comparable in energy with the lowest L ← M transition near $n = 4$, and as the M ← L transition usually has a large low-frequency tail,[8] it is possible that this transition overlaps the intervalence transition. Further experimental work is required in order to characterize the observed bands, and it is also desirable that the comproportionation constant be determined experimentally.

Nitrobenzene is an unusual solvent, and it is possible that there are specific solvent effects on the observed intervalence M ← M spectra. The LUMO level of free nitrobenzene is ≈0.8 eV more stable than the LUMO level of 4,4′-bipyridine (estimated from one-electron reduction potentials[18,19]), and thus one would expect the metal to solvent (S ← M) transition to lie between the L ← M and M ← M transitions. Typical aqueous S ← M intensities[20] are of the order of $\epsilon = 100$–1000 M^{-1} cm^{-1}, and this could be sufficient to cause additional absorption in the region of the intervalence band. In addition, this low energy of the S ← M transition allows the possibility of a solvent superexchange enhancement of the intermetallic coupling, similar to that suggested[21] for photoinduced electron transfers in benzene solution. Further, there is the possibility that supramolecular effects are operative. Nitro groups can be accommodated in the electron-deficient holes beween the ammine ligands and thus experience significant interaction with the metal d orbitals. Recently, a strong interaction comparable to the Ru–N coupling was discovered[22] between bipyridine ligand and close parallel ortho-disubstituted benzene groups in crown ether "supramolecules", which suggests that a significant interaction could also occur between bipyridyl and nitrobenzene in solution. Contributions from all of the above effects would be strongly packing- and thus n-dependent and might account for the observed spectral band shapes and couplings.

While specific solvent effects of the above kind present interesting possibilities, it is not possible at this stage to form estimations of their importance (if any). To verify their existence, one needs to repeat and verify the existing experiments in nitrobenzene (and also in D_2O) and also to perform experiments to determine accurately the coupling in similar solvents (e.g. nitromethane) that do not provide such specific effects.

It is of great advantage to the development of theoretical models[23-26] for long-distance electron-transfer processes if the effective intermetallic coupling within the bis(pentaammineruthenium) complexes of the α,ω-dipyridyl *trans*-polyenes could be measured in one inert solvent over as large of a range of n as

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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[pyridine]-*N*:*N*′]]diruthenium(5+), 118494-84-1.

Contribution from the Fachbereich Chemie, Universität Marburg, Hans-Meerwein-Strasse, D-3550 Marburg, West Germany, and IBM Scientific Center, Tiergartenstrasse 15, D-6900 Heidelberg, West Germany

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

G. Frenking* and W. Koch

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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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* To whom correspondence should be addressed at Universität Marburg.

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