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Theoretical Investigation of the Dihydrogen Bond Linking MH_2 with HCCRgF (M = Zn, Cd; Rg = Ar, Kr)

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An ab initio computational study of the properties of four linear dihydrogen-bonded complexes pairing MH_2 (M = Zn, Cd) with HCCRgF (Rg = Ar, Kr) was undertaken at the MP2/DGDZVP level of theory. The calculated complexation energies of the linear complexes vary between 6.5 kJ/mol for M = Zn to 8.5 kJ/mol for M = Cd. Equilibrium interatomic H···H distances are roughly 2.07 Å for all four complexes. The red shifts of the H−C stretching frequency of HCCRgF correlate nicely with the interaction energies.

1. Introduction

The subject of dihydrogen bonds has received a great deal of attention lately.[1−6] The dihydrogen bond is an attractive H···H interaction, arising from the close approach of a protonic H atom and a hydridic H atom.[7] In a parallel vein, metal hydrides are of considerable importance in chemical synthesis as intermediates in catalytic hydrogenation reactions. Transition-metal atoms react with dihydrogen to produce metal dihydrides or dihydrogen complexes, and these may be trapped in solid matrix samples for infrared spectroscopic study.[8]

It has been shown previously that metal hydrides are capable of forming dihydrogen bonds.[9−12] Recently, we have published a series of papers concerning dihydrogen-bonded complexes of metal hydrides with certain rare gas derivatives.[13−15] We turn our attention now to the potential interactions involving the alkynic H of rare-gas systems HC≡CRgF. In the absence of an experimental search for the title complexes up to the present, a theoretical analysis of their properties would appear to be in order. The present work thus reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of the title complexes for the first time.

2. Computational Details

Calculations were performed using the Gaussian03 system of codes.[16] Geometry optimizations and frequency calculations were performed at the MP2 level using DGDZVP basis set.[17] Harmonic vibrational frequency calculations were performed, which confirm the predicted structures as minima in the potential energy surfaces (PESs) of the title complexes The charge distribution has been analyzed by the natural bond orbital (NBO)[18] partitioning scheme at the MP2/DGDZVP level. The counterpoise (CP) method[19] was used to correct basis set superposition error (BSSE) in the calculation of the binding energy.

3. Results and Discussion

Association of the linear HCCRgF molecules (Rg = Ar, Kr) with linear MH_2 (M = Zn, Cd) subunits[8] leads to the similarly linear $C_{\infty v}$ complexes HMH···HCCRgF, which were calculated to be minima at the MP2/DGDZVP level of theory. Completely optimized geometries for all species are reported in Figure 1.

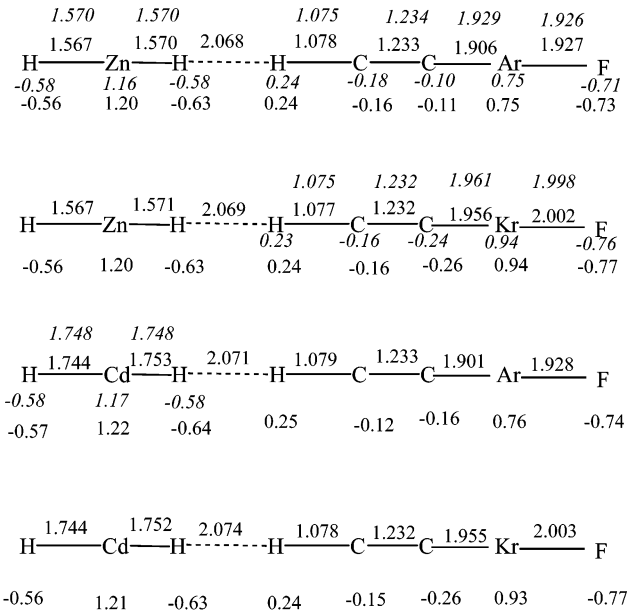

Figure 1. MP2/DGDZVP geometries (Å) and NBO atomic charges (e) of HMH···HCCRgF complexes. Results for monomers in italics.

The computed complexation energies of the linear dihydrogen-bonded complexes are about 6.5 kJ/mol for the Zn complexes, as compared to the larger 8.5 kJ/mol for those that contain Cd, as indicated in Table 1. The nature of the rare gas atom has little effect on this quantity, although there is a slight preference for Kr over Ar. This 0.3 kJ/mol difference, however, is probably within the margin of error of the computational method.While quantitatively different, the interaction energies computed without BSSE correction obey the same trends.

The NBO atomic charges displayed in Figure 1 reveal relatively minor changes upon complexation. The process seems to make the “hydridic” H of the HMH, that is, the bridging proton, somewhat more negative by an amount of about 0.05.

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TABLE 1: Binding Energies of MH_2 with HCCRgF and Other Properties at MP2/DGDZVP Level

complex	ΔE kJ/mol	CC kJ/mol	$\Delta E^{cp,a}$ kJ/mol	R(H••H) Å	ν(H•••H) cm^{-1}	$\Delta\nu$(H−C) cm^{-1}
HZnH•••HCCArF	−10.01	3.61	−6.40	2.068	51	−41
HZnH•••HCCKrF	−10.32	3.63	−6.69	2.069	48	−42
HCdH•••HCCArF	−11.36	3.10	−8.26	2.071	44	−56
HCdH•••HCCKrF	−11.67	3.11	−8.56	2.074	41	−56

[a] ΔE^{cp} refers to interaction energy after counterpoise correction, ΔE + CC.

TABLE 2: MP2/DGDZVP Unscaled Vibrational Frequencies (cm^{-1}) of Complexes

	HZnH••• HCCArF	HZnH••• HCCKrF	HCdH••• HCCArF	HCdH••• HCCKrF
ν_1	15(π)	16(π)	16(π)	17(π)
ν_2	51(σ)	48(σ)	44(σ)	41(σ)
ν_3	70(π)	92(π)	70(π)	89(π)
ν_4	134(π)	141(π)	129(π)	137(π)
ν_5	253(σ)	311(π)	257(σ)	311(π)
ν_6	309(π)	399(σ)	310(π)	400(σ)
ν_7	557(σ)	516(σ)	553(σ)	515(σ)
ν_8	650(π)	656(π)	561(π)	561(π)
ν_9	694 (π)	711 (π)	689 (π)	711 (π)
v_{10}	1906(σ)	1906(σ)	1718(σ)	1718(σ)
ν_{11}	1910(σ)	1909(σ)	1736(σ)	1736(σ)
ν_{12}	2000(σ)	2023(σ)	2000(σ)	2022(σ)
ν_{13}	3412(σ)	3415(σ)	3397(σ)	3400(σ)

TABLE 3: MP2/DGDZVP Vibrational Frequencies (cm^{-1}) of Monomers

frequency	HCCArF	HCCKrF	HZnH	HCdH
ν_1	72(π)	105(π)	659(π)	562(π)
ν_2	227(σ)	310(π)	1891(σ)	1704(σ)
ν_3	302(π)	390(σ)	1898(σ)	1726(σ)
ν_4	570(σ)	520(σ)		
ν_5	610(π)	634(π)		
ν_6	1999(σ)	2027(σ)		
ν_7	3453(σ)	3457(σ)		

TABLE 4: Intermolecular H•••H Stretching Frequency (cm^{-1}) and Changes in Stretching Frequencies of Monomers Caused by Complexation at MP2/DGDZVP Level

nature	HZnH••• HCCArF	HZnH••• HCCKrF	HCdH••• HCCArF	HCdH••• HCCKrF
ν (H•••H)	51	48	44	41
HMH (sym)	15	15	15	14
HMH (asym)	12	11	12	12
H−C	−41	−42	−56	−56
C−C	1	-3	1	−5
C−Rg	26	10	30	11
Rg−F	−23	−4	−26	−4

TABLE 5: Calculated Absolute ^1H Chemical Shielding (ppm) of the Monomers and Complexes at the MP2/DGDZVP Level with Pertinent Atom Shown in Bold

system	HM**H**•••HCCRgF	HMH•••**H**CCRgF
HZnH	27.62	
HCdH	27.27	
HCCArF		29.73
HCCKrF		29.64
HZnH•••HCCArF	28.13	28.87
HZnH•••HCCKrF	28.13	28.81
HCdH•••HCCArF	27.78	28.63
HCdH•••HCCKrF	27.79	28.58

This electron density is drawn from the metal atom, as the total charge assigned to the HMH molecule is essentially unchanged. In other words, there is little if any charge transfer between the two subunits. Within the confines of the HCCRgF molecule, very little change is caused by complexation with HZnH. The HCdH molecule, on the other hand, does induce a certain amount of polarization of the C≡C bond, at least within HCCArF. The HC carbon atom, for example, becomes more positive by 0.06, and the other C becomes more negative by a similar amount.

The harmonic vibrational frequencies of the complexes and their constituent monomers are listed in Tables 2 and 3, respectively. The calculated frequencies confirm (there is no imaginary frequency) that structures with $C_{\infty v}$ symmetry are minima in the potential energy surfaces (PESs) of the title complexes. The second frequency, ν_2, corresponds to the intermolecular stretching frequency, commonly referred to as ν_σ. This set of frequencies is repeated in the first row of Table 4, which reports in the ensuing rows the *changes* in the stretching frequencies of the monomers that result from the complexation. One may note first that the symmetric and asymmetric stretches of the HMH molecule are increased by 12−15 cm^{-1}, with little sensitivity to the identity of the molecules. Much more dependent upon the particular interaction are the HCCRgF vibrations. Starting with the H−C stretch, this frequency drops by about 40 cm^{-1} for the two Zn complexes and by 56 cm^{-1} for those involving Cd. In contrast, the C≡C stretch is rather stable, to within 5 cm^{-1}. The C−Rg stretching frequency rises by 30 cm^{-1} or so for HCCArF but by only one-third that amount for the Kr analogue. The HCCKrF molecule is likewise much less perturbed with regard to the Rg−F stretch; see the final row of Table 4.

The H•••H intermolecular distances reported in Figure 1 all fall into a narrow range of 2.068−2.074 Å. The bond lengths in Figure 1 pinpoint those that undergo the greatest change. The peripheral H−M bond is shortened by 0.03−0.04 Å upon complexation, while the other M−H bond, involving the bridging hydrogen, is stretched in HCdH (but not in HZnH). The H−C bond of the partner molecule also elongates by 0.02−0.04 Å. The bond which undergoes the largest change is the C−Rg distance, particularly for Rg = Ar, wherein C−Ar contracts by 0.028 Å in the HCdH•••HCCArF complex.

The absolute ^1H chemical shieldings of the hydrogen donor and acceptor atoms were calculated at the MP2/DGDZVP level for monomers and complexes are listed in Table 5. Complexation leads to an increase of the chemical shielding of the hydrogen atom attached to the transition metal by some 0.5 ppm, regardless of system. In contrast, the alkyne H shielding undergoes a decrease. The magnitude of this decrease is equal to 0.8 ppm for the two complexes containing Zn and 1.1 ppm for the two Cd analogues.

The results of the present study first confirm the nature of the intermolecular interaction as a dihydrogen bond. Perusal of the data reported in Table 1 suggests that the red shift of the H−C intramolecular stretching frequency of the HC≡CRgF subunit represents the strongest indicator of the energetic strength of the intermolecular interaction, superior to either the intermolecular distance or the intermolecular stretching frequency. The data further indicate that these dihydrogen-bonded complexes ought to be experimentally observable in the gas phase, certainly at low temperature. It is our hope that the present study may motivate experimentalists to search for the title complexes, perhaps by matrix isolation techniques.

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