Table I. Reaction Exothermicities (kcal/mol)

	(1)	(2a)	(2b)	(3)	(4)
RHF/6-31G*	6.3	-30.0	-17.3	-54.5	-36.2
RHF/6-31++G**	-0.6	-30.3	-22.3	-53.4	-40.6
MP2/6-31++G**	-5.5	-24.2	-12.1	-27.3	-32.0
MP3/6-31++G**	-3.9	-25.7	-17.8	-37.8	-35.3
MP4/6-31++G**	-5.7	-23.2	-11.7	-26.6	-37.3

Generally speaking, the MP2 values reproduce the MP4 results very well (reaction 4 is the worst case). The quality of the basis affects only reactions 1 and 2b, while inclusion of electron correlation at the MP2 level can have a dramatic effect.

We have performed one MP4 calculation on the ring form of reaction 1. This ring lies -40.9, -41.0, -46.6, and -44.9 kcal/mol below the reactants at the RHF, MP2, MP3, and MP4 levels with the diffuse basis set. The MP4 calculation required 17 cpu days on a Celerity minicomputer, and thus consistent application of MP4 to the present problem is prohibitive. Fortunately, MP2 is shown to give fairly reliable agreement with the full MP4 tests that were done.

Conclusions

The reactions of HCSi⁻ involve the initial formation of stable four-membered rings, of the type proposed by Damrauer, DePuy, Barlow, and Gronert.[1] However, these do not undergo synchronous cleavage to the observed products; instead, they open at one side leading to two different acyclic forms. Either of these can break a second bond, leading to the experimentally observed products.

Ab Initio Studies on the Hydrogen-Bonded Complexes between Hydrogen Fluoride and Hydroxylamine

Richard E. Brown,*,† Qingguo Zhang,† and Rodney J. Bartlett‡

Contribution from the Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931, and Quantum Theory Project, University of Florida, Gainesville, Florida 32611. Received January 17, 1991

Abstract: The minimum-energy geometries for the complexes between hydrogen fluoride and hydroxylamine (HF)₁H₂NOH and (HF)₂H₂NOH were studied at the Hartree–Fock level and also at the second-order level in many-body perturbation theory (MBPT(2)) in order to estimate the effects of electronic correlation. The novel ring structures observed recently for these hydrogen-bonded complexes were confirmed. The 1:1 complex contains a loosely bound ring structure with a strong N–HF bond and weak long HF–HO bond. An association enthalpy of about -6 to -9 kcal/mol is predicted. For the 1:2 complex, a second HF molecule is inserted into the ring between the first HF moiety and the HO group. This complex exhibits three strong hydrogen bonds and a correspondingly larger association enthalpy of approximately -17 to -19 kcal/mol. The harmonic vibrational analysis at the MBPT(2) level supports most of the assumptions made in the analysis of the FTIR studies.

Introduction

Of the weak interactions, hydrogen bonding is the strongest. It is important in a wide variety of natural phenomena from the formation of interstellar clouds to determining the conformation and properties of biological compounds. Studies on isolated hydrogen-bonded complexes can provide new information on how hydrogen bonding affects the properties of molecular complexes. With the development of new theoretical and experimental methods, increasingly larger and more complex systems are being studied. One such example is the (HF)ₙ–H₂NOH complexes.

The hydrogen fluoride–hydroxylamine complexes represent a particularly interesting and difficult problem. Recently Lascola and Andrews have identified such complexes and proposed that they have cyclic structures.[1] They opted to use argon matrix isolation FTIR spectroscopy at temperatures of 12–25 K. This was dictated by the instability of hydroxylamine, which dissociates to water and ammonia. The possible presence of such dissociation products made the analysis of the FTIR data particularly difficult. Both HF and H₂NOH are capable of forming strong hydrogen bonds. Hydroxylamine has two electron-rich basic sites, the

nitrogen and oxygen. Some suspicion exists that the basicity of the nitrogen may be sufficiently reduced by the oxygen that the latter might become the preferred site of hydrogen atom attachment. The identification of the primary binding site was one of the major concerns of Lascola and Andrews.

The FTIR spectra indicated that both of the complexes (H-F)₁NH₂OH (the 1:1 complex) and (HF)₂NH₂OH (the 1:2 complex) are stable. Both were of a cyclic nature. The primary binding site for HF attachment was the more basic nitrogen atom. However, for the 1:1 complex, the F atom formed a long secondary hydrogen bond with the hydroxyl hydrogen as indicated by the perturbation to the OH stretching and NOH bending motions. The large blue shift to the NH₂ wagging mode and the nature of the perturbation to the HF stretching vibration indicate that the nitrogen is the primary binding site, not the oxygen. Isotopic substitution on both monomers supports these conclusions as well as the cyclic geometry of the 1:1 complex. The attachment of the second HF molecule is also of considerable interest. Lascola and Andrews speculate that the second HF molecule inserts into the ring to give a seven-member ring with the linkage –N--H–F--H–F--H–O-.[1] The evidence for this structure is however not

---

† Michigan Technological University.
‡ University of Florida.

(1) Lascola, R.; Andrews, L. *J. Am. Chem. Soc.* **1987**, *109*, 4765.

Table I. Computed Properties of Monomers[a]

	SCF 6-31G	MBPT(2) 6-31G	SCF 6-31G*	MBPT(2) 6-31G*	SCF 6-31G**	MBPT(2) 6-31G**
			Hydrogen Fluoride			
E (SCF)	−99.983 43	−99.982 72	−100.002 91	−100.002 31	−100.011 69	−100.011 16
E [MBPT(2)]		−100.113 00		−100.184 16		−100.196 80
R (Å)	0.9209	0.9469	0.9108	0.9169	0.9005	0.9212
q_H	0.48	0.49	0.517	0.517	0.387	0.398
μ (D)	2.30	2.34	1.97	2.01	1.94	1.98
			Hydroxylamine			
E (SCF)	−130.925 56	−130.920 96	−130.978 84	−130.976 16	−130.991 66	−130.989 35
E [MBPT(2)]		−131.165 04		−131.330 18		−131.360 35
R_{NH} (Å)	0.9985	1.0226	1.0022	1.0209	1.0016	1.0163
R_{NO} (Å)	1.4345	1.5125	1.4037	1.4516	1.4024	1.4493
R_{OH} (Å)	0.9507	0.9804	0.9466	0.9710	0.9428	0.9637
θ_{HNO}	106.3	103.5	104.7	102.9	105.0	101.2
θ_{NOH}	106.4	102.2	104.2	101.4	104.4	103.0
Φ_{HNOH}	120.5	122.9	124.0	125.4	123.8	125.5
μ (D)	0.92	1.00	0.68	0.76	0.68	0.76
$q_H{}^b$	0.34	0.35	0.35	0.35	0.28	0.29
q_N	−0.49	−0.51	−0.52	−0.53	−0.39	−0.39
q_O	−0.62	−0.61	−0.63	−0.63	−0.54	−0.55
$q_H{}^c$	0.43	0.43	0.46	0.46	0.36	0.36

[a] Atomic units are used unless specified. [b] Ammino hydrogen. [c] Hydroxyl hydrogen.

as convincing. Attachment to the H_2NO moiety on the side opposite to the first HF molecule is also a possibility that will be investigated here.

Considering the experimental problems with dissociation products, the availability of multiple bonding sites, and the unexpected cyclic structure of these particular complexes, an independent theoretical study is warranted.

Method

Some investigations have shown that hydrogen-bonding effects can be reliably studied at the Hartree–Fock (HF) or self-consistent field (SCF) level if a sufficiently complete basis set is used.[2–6] Results from studies on the structure and bonding energies of such complexes can be very sensitive to the quality of the basis set, with or without the inclusion of correlation effects. At the SCF level, the indications are that the basis should be of a triple-ζ quality and include two sets of polarization functions and one set of diffuse functions, i.e., a 6-311++G** basis. See work by Szalewicz et al.,[7] Latajka and Scheiner,[6] Frisch et al.,[5] and Dykstra et al.[8]

This work extends the SCF method to include correlation by using the many-body perturbation theory/coupled cluster method (MBPT/CC).[9–12] Such an approach can reliably predict enthalpies of reaction, binding energies, and association energies to within a few kilocalories per mole[9] with use of basis sets of at least double-ζ plus polarization quality. Of some concern is how basis set deficiencies in the SCF and correlation components of the wave function affect the structure and energy of weakly bonded complexes. A false perception of accuracy can be obtained when these two effects tend to cancel.[5]

The MBPT/CC method avoids the problem of incorrect scaling with size, or size inextensivity. This is particularly important when interpreting the energy differences of weakly bonded complexes and their component monomers, as a size-extensive method guarantees correct separation of a closed-shell complex into closed-shell fragments.[9] Fur-
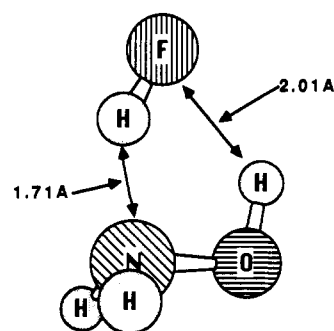

Figure 1. Structure of the HF–NH₂NOH dimer optimized at the MBPT(2)/6-31G** level of theory.
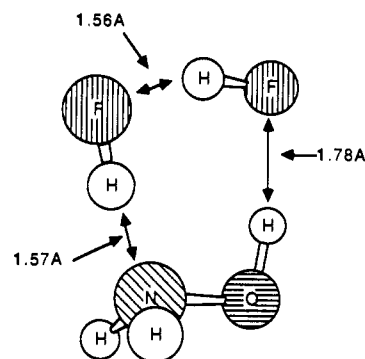

Figure 2. Structure of the (HF)₂NH₂NOH trimer optimized at the MBPT(2)/6-31G* level of theory.

thermore, this approach treats the supermolecule cluster on the same level as the component monomers at a given level of the many-body wave function.[9,12,13]

However, an ab initio method is still subject to basis set superposition errors (BSSE).[14] Counterpoise (CP) estimates of the BSSE will be made here on selected results to assess the magnitude of these errors. Although the BSSE can have either sign,[7] the CP estimates determined here are all positive.

A hierarchy of calculations will be used here where crude calculations (SCF with small basis sets) are followed by more exact approaches (SDQ-MBPT(4) and full MBPT(4) with a 6-311++G** basis). Basis sets used are the STO-3G, 6-31G, 6-31G*, 6-31G**, 6-31++G*, and 6-311++G** sets. Geometry optimizations will be performed at the SCF

(2) Curtiss, L. A.; Pople, J. A. *J. Mol. Spectrosc.* **1973**, *48*, 413; **1975**, *55*, 1; **1976**, *61*, 1.

(3) Hobza, P.; Carsky, P.; Zahradnik, R. *Collect. Czech. Chem. Commun.* **1979**, *44*, 3458.

(4) Gaw, J. F.; Yamaguchi, Y.; Vincent, M. A.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1984**, *106*, 3133.

(5) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 2279.

(6) Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1987**, *87*, 5928.

(7) Szalewicz, K.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3662.

(8) Dykstra, C. E.; Liu, S.-Y.; Malik, D. J. *Adv. Chem. Phys.* **1989**, *75*, 37. Liu, S.-Y.; Dykstra, C. E.; Malik, D. J. *Chem. Phys. Lett.* **1986**, *130*, 403.

(9) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697. Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

(10) Kelly, H. P. *Adv. Chem. Phys.* **1969**, *14*, 129.

(11) Cizek, J. *J. Chem. Phys.* **1966**, *45*, 4256. Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(12) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561. Kucharski, S. A.; Bartlett, R. J. *Adv. Quantum Chem.* **1986**, *18*, 281.

(13) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(14) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

Table II. Computed Properties of the 1:1 Complex[a]

	SCF 6-31G	MBPT(2) 6-31G	SCF 6-31G*	MBPT(2) 6-31G*	SCF 6-31G**	MBPT(2) 6-31G**
E (SCF)	-230.929 30	-230.923 57	-230.998 79	-230.994 54	-231.019 99	-231.016 26
E [MBPT(2)]	-231.303 28			-231.538 27		-231.580 16
R_{NO} (Å)	1.4335	1.5090	1.3987	1.4426	1.3979	1.4402
R_{OH} (Å)	0.9557	0.9880	0.9530	0.9782	0.9466	0.9703
R_{NH} (Å)	0.9996	1.0220	1.0025	1.0206	1.0020	1.0158
θ_{HNO}	106.4	101.4	105.4	104.3	105.8	104.5
θ_{NOH}	106.4	104.6	104.3	100.8	104.4	100.6
Φ_{HNOH}	120.8	122.3	123.4	124.2	123.2	124.1
$\theta_{ONH'}$[b]	95.9	94.0	95.7	94.0	95.4	93.6
$R_{NH'}$ (Å)	1.766	1.7064	1.8373	1.7245	1.8439	1.7136
$R_{H'F}$ (Å)	0.9455	0.9846	0.9293	0.9660	0.9177	0.9515
$R_{F'H}$ (Å)[d]	2.2207	2.0684	2.2033	1.9695	2.2040	2.0130
$\theta_{NH'F}$	146.9	145.7	145.8	144.2	146.2	146.1
μ (D)	3.25	3.48	2.82	3.02	2.77	2.99
q_H[c]	0.37	0.38	0.37	0.38	0.30	0.31
q_N	-0.57	-0.61	-0.58	-0.60	-0.44	-0.46
q_O	-0.59	-0.58	-0.62	-0.62	-0.52	-0.53
q_H[d]	0.44	0.45	0.47	0.48	0.37	0.38
$q_{H'}$	0.54	0.56	0.57	0.56	0.42	0.45
q_F	-0.56	-0.58	-0.57	-0.58	-0.43	-0.47

[a] Atomic units are used except where specified. [b] H' denotes hydrogen in the HF moiety. [c] Ammino hydrogen. [d] Hydroxyl hydrogen.

and MBPT(2) second-order levels by using sets up to 6-31G* and 6-31G** quality. At the most reliable geometries, the SDQ-MBPT(4) and full MBPT(4) fourth-order energies of the monomers and clusters will be determined in order to get accurate values for the association enthalpies.

In order to verify the experimental vibrational assignments, the harmonic frequencies and normal coordinates are calculated. To better interpret vibrational spectra, the normal coordinates are then transformed from Cartesian displacement coordinates to internal displacement coordinates.

Results

The numerical results are presented in Tables I–VIII. For all molecules, the geometries were optimized at the SCF and MBPT(2) levels by using first a STO-3G or 6-31G basis and then the 6-31G* and 6-31G** basis sets. Some results are tabulated in Table I, II, and III for the monomers HF and H_2NOH, the 1:1 complex, and the 1:2 complex, respectively. Table IV lists the harmonic vibrational frequencies and intensities of each molecule as well as including some experimental data. These vibrational results for the 1:1 complex are at the MBPT(2)/6-31G** level, and those for the 1:2 complex are at the SCF/6-31G* level. The SCF frequencies were scaled by a factor of 0.89. Figures 1 and 2 illustrate the geometries of the 1:1 and 1:2 complexes.

At the MBPT(2) geometry, the energies of all molecules were then determined with use of the 6-31++G* and the 6-311++G** basis sets. These are summarized in Table V, and the corresponding association enthalpies (the enthalpy of the complex less those of the constituent monomers) are given in Table VI. These enthalpies include the thermal effects for translational, rotational, and vibrational motions at 298.2 K. In selected cases, the counterpoise (CP) estimates of the BSSE are also reported. It is important to note the CP method typically but not always[7] overestimates the BSSE and may possibly induce a larger error than omitting the correction. Hence, it will tend to lower the magnitude of the association energy so as to underestimate the stability of the complexes. For example, with the 1:1 complex, the CP corrections to the association enthalpies were about 0.8, 2.3, 2.3, and 2.5 kcal/mol at the SCF, MBPT(2), SDQ-MBPT(4), and MBPT(4) levels, respectively, for the 6-311++G** basis. Of the basis sets tested for the 1:1 complex, the 6-31G* basis showed the largest CP correction, with values typically twice that of the 6-311++G** basis. More detailed studies by Schwenke and Truhlar[15] and Loushin, Liu, and Dykstra[16] give similar results for hydrogen-bonded systems. For the 1:2 complex, the SCF and

Table III. Computed Properties of the 1:2 Complex[a]

	SCF 6-31G	MBPT(2) 6-31G	SCF 6-31G*	MBPT(2) 6-31G*
E (SCF)	-330.938 63	-330.931 91	-331.022 97	-331.017 02
E [MBPT(2)]		-331.447 23		-331.751 83
R_{NO} (Å)	1.4334	1.5034	1.3964	1.4376
R_{OH} (Å)	0.9603	0.9943	0.9528	0.9838
R_{NH} (Å)	1.0010	1.0027	1.0033	1.0216
θ_{NOH}	108.1	104.4	105.7	103.0
θ_{HNO}	105.9	104.1	105.4	104.5
Φ_{HNOH}	121.7	122.7	123.7	124.2
$R_{NH'}$ (Å)	1.6057	1.5066	1.7215	1.5688
$R_{H'F'}$ (Å)	0.9772	1.0406	0.9474	1.0029
$R_{H''F''}$ (Å)	0.9399	0.9795	0.9264	0.9647
$R_{H''F'}$ (Å)	1.6452	1.5663	1.6916	1.5608
$R_{F''H}$ (Å)[d]	1.8661	1.7924	1.9254	1.7813
$\theta_{ONH'}$[b]	111.3	111.0	113.0	112.3
$\theta_{NH'F'}$	166.9	168.6	167.7	168.8
$\theta_{H'F'H''}$	101.0	98.6	96.1	94.4
$\theta_{F'H''F''}$	146.9	152.0	153.1	157.7
μ (D)	3.62	4.07	3.18	3.61
q_H[d]	0.39	0.39	0.38	0.38
q_N	-0.61	-0.65	-0.60	-0.60
q_O	-0.60	-0.58	-0.63	-0.62
q_H[c]	0.47	0.49	0.49	0.49
$q_{H'}$	0.58	0.59	0.57	0.57
$q_{F'}$	-0.60	-0.62	-0.58	-0.59
$q_{H''}$	0.53	0.54	0.55	0.55
$q_{F''}$	-0.54	-0.56	-0.56	-0.57

[a] Atomic units are used except where specified. [b] H' and F' denote atoms in first HF. [c] H'' and F'' denote atoms in second HF. [d] Ammino hydrogen. [e] Hydroxyl hydrogen.

MBPT(2) CP corrections with the 6-311++G** basis are, respectively, 0.6 and 1.4 kcal/mol, again smaller than the corresponding values of 1.4 and 3.7 kcal/mol for the 6-31G* basis. With few exceptions, for a particular basis, the non-SCF methods showed similar CP corrections that were typically about 2–3 times that of the SCF values.

Table VII gives the SCF population analyses for the molecules by using the 6-311++G** basis at the MBPT(2) optimum geometry. Finally, Table VIII details the calculated and experimentally known perturbations to the monomer vibrational frequencies as observed in both the 1:1 and 1:2 complexes.

Monomers HF and H_2NOH. These molecules have been studied extensively by other investigators and so will need little comment here.[17-22] Some calculations were completed here in order to

(15) Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *82*, 2418.
(16) Loushin, S. K.; Liu, S.-Y.; Dykstra, C. E. *J. Chem. Phys.* **1986**, *84*, 2720.

(17) Frisch, M. J.; Pople, J. A.; Del Bene, J. E. *J. Phys. Chem.* **1985**, *89*, 3664.

Table IV. Harmonic Vibrational Analysis of the Monomers and Complexes at the MBPT(2)/6-31G** and SCF/6-31G* Levels[a]

molecule	symmetry, mode	ω [MBPT(2)]	ω (exptl)	ω (SCF)
HF				
	A′, HF stretch	4189 (82)	3962	3880 (141)
H₂NOH				
	A″, H₂NOH torsional	407 (198)	376	404 (223)
	A′, NO stretch	954 (10)	895	1000 (16)
	A′, NH₂ wag	1192 (155)	1117	1139 (180)
	A″, NH₂ rock	1348 (0)	1311	1318 (0)
	A′, NOH bend	1430 (22)	1351	1388 (31)
	A′, NH₂ bend + NO stretch	1703 (19)	1599	1654 (21)
	A′, NH stretch	3530 (2)	3290	3307 (2)
	A″, NH stretch	3635 (0)	3353	3389 (0)
	A′, OH stretch	3893 (36)	3635	3665 (60)
(HF)H₂NOH				
	A′, HF libration	201 (7)		129 (7)
	A″, HF libration	293 (1)		246 (1)
	A′, NH′ stretch	307 (15)		247 (9)
	A″, H₂NOH torsional	507 (71)	368	413 (64)
	A″, HF libration	909 (203)	780	732 (288)
	A′, NO stretch + HF stretch	962 (60)	865	1022 (14)
	A′, HF libration + NO stretch	1018 (172)	885	807 (261)
	A′, NH₂ wag	1221 (217)	1163	1162 (208)
	A″, NH₂ rock	1326 (0)		1307 (0)
	A′, NOH bend	1534 (39)	1385	1448 (37)
	A′, NO stretch + HNO, NH₂ bend	1698 (21)		1648 (23)
	A′, HF stretch + NH₂ bend	3525 (522)	3042	3524 (541)
	A″, NH₂ stretch	3647 (6)		3394 (7)
	A′, NH₂ stretch + HF stretch	3551 (135)		3314 (7)
	A′, OH stretch	3806 (220)	3612	3630 (245)
(HF)₂H₂NOH				
	A″, H–N–H′–F′H″ deformatn			53 (12)
	A′, H′F′H″, NH′F′, H′F′H″ bend			125 (10)
	A′, H₂N wag, NH′F′ bend			181 (0)
	A′, H₂N wag, F′H″ stretch			234 (7)
	A′, H₂N wag, NH′ stretch			267 (17)
	A″, NH₂ scissors, ring deformatn			285 (0)
	A″, H′F′, H″F″ libration			495 (5)
	A″, H″F″ libration			557 (210)
	A′, H′F′ libration			697 (323)
	A″, H′F′ libration			878 (300)
	A′, NO + F′H″ stretch			999 (78)
	A′, NO – F′H″ stretch			1047 (29)
	A′, NH₂ wag, ring deformatn			1198 (218)
	A″, NH₂ rock, ring deformatn			1310 (1)
	A′, NOH bend, NO stretch			1478 (34)
	A′, NO stretch, NH′F′, H′F′H″ bend			1648 (23)
	A′, H′F′ stretch			3172 (1230)
	A′, NH₂ stretch			3309 (0)
	A″, NH₂ stretch			3384 (9)
	A′, OH stretch			3584 (412)
	A′, H″F″ stretch			3634 (595)

[a]The SCF/6-31G* frequencies are scaled by a factor of 0.89. Frequencies are given in inverse centimeters, and the relative intensities (km/mol) are given in parentheses. The mode assignments, particularly for the low-frequency ring deformations, are approximate.

provide comparisons to the results for the complexes and to assess the relative accuracy of the methods used. The second-order method gave longer bond lengths, smaller bond angles, and a larger dihedral angle. Correlated methods have special basis set requirements to adequately include radial and angular correlation. Recent results indicate that the MBPT(2) method with either the 6-31G* or 6-31G** basis not only predicts the geometrical parameters of the monomer units accurately, but also can predict the association energies of the dimers to within a few kilocalories per mole.[17] It was observed that the geometries at the SCF/6-31G* level of theory were almost unchanged upon increasing the

basis size by adding additional polarization functions and diffuse functions on the hydrogens. Other properties such as the dipole moments and vibrational frequencies were less accurately predicted. For the first- and second-row hydrides, the association energies of the dimers for the 6-31G* and 6-31+G* basis sets were within 0.5 kcal/mol of each other, except for (HF)₂, which showed a 2.5 kcal/mol difference. This work will focus on the MBPT-(2)/6-31G** geometry for the 1:1 complex and the MBPT(2)/6-31G* geometry for the 1:2 complex but will use larger basis sets at these geometries for the determination of the association energies.

MBPT(2) harmonic vibrational frequencies with basis sets of polarized double-ζ quality are typically accurate to about 5%.[23] For H₂NOH, the MBPT/6-31G** harmonic vibrational assignments agree well with the experimental counterparts except for the sixth mode (NH₂ bend), which showed strong mixing with the NO stretch.

(18) Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950. Herzberg, G. *Infrared and Raman Spectroscopy*; Van Nostrand Reinhold: New York, 1945.

(19) Schmidt, M. W.; Yabushita, S.; Gordon, M. S. *J. Phys. Chem.* **1984**, *88*, 382.

(20) Riddell, F. C. *Tetrahedron* **1981**, *31*, 849.

(21) Radom, L.; Hehre, W.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 3271.

(22) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1988**, *92*, 2155 and references therein.

(23) Bartlett, R. J.; Stanton, J. F.; Watts, J. D. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J., Ed.; JAI Press: Greenwich, CT, in press.

5252 *J. Am. Chem. Soc., Vol. 113, No. 14, 1991*

Brown et al.

Table V. Calculated Energies of the Monomers and the 1:1 and 1:2 Complexes with Various Methods

method	HF	H$_2$NOH	(HF)-H$_2$NOH	(HF)$_2$-H$_2$NOH
		SCF		
6-31G[a]	−99.98343	−130.92556	−230.92930	−330.93863
6-31G*[a]	−100.00291	−130.97884	−230.99879	−331.02297
6-31G**[a]	−100.01169	−131.99166	−231.01999	
6-31++G*[b]	−100.01443	−130.98371	−231.01120	−331.04119
6-311++G**[b]	−100.05173	−131.02998	−231.09305	−331.15740
6-311++G**[c]	−100.05261	−131.03073	−231.09484	
		MBPT(2)		
6-31G[a]	−100.11300	−131.16504	−231.30328	−331.44723
6-31G*[a]	−100.18416	−131.33017	−231.53827	−331.75183
6-31++G*[c]	−100.19670	−131.36035	−231.58016	
6-31++G*[c]	−100.20301	−131.34042	−231.56284	−331.78802
6-311++G**[b]	−100.27857	−131.42903	−231.72466	−332.02193
6-311++G**[c]	−100.27887	−131.42915	−231.72515	
		SDQ-MBPT(2)		
6-31G*[b]	−100.18660	−131.34231	−231.55056	−331.76376
6-31++G*[b]	−100.20660	−131.35755	−231.58192	−331.80891
6-311++G**[b]	−100.28085	−131.44462	−231.74111	−332.03926
6-311++G**[c]	−100.28120	−131.44476	−231.74174	
		MPBT(4)		
6-311++G**[c]	−100.28622	−131.45805	−231.76109	

[a] Calculated at the optimum geometry for the method. [b] Determmfined at the MPBT(2)/6-31G* optimum geometry. [c] Determined at the MBPT-(2)/6-31G** optimum geometry.

Table VI. Association Enthalpies (kcal/mol)[a]

method	comment	(HF)H$_2$NOH	(HF)$_2$H$_2$NOH
SCF/6-31G	b	−10.7	−25.3
SCF/6-31G*	b	−8.7 (−5.7)	−20.3 (−18.9)
SCF/6-31G**	b	−8.4	
SCF/6-31++G*	c	−6.2 (−4.9)	−14.3 (−11.8)
SCF/6-311++G**	c	−5.1	−11.3 (−10.7)
SCF/6-311++G**	d	−5.2 (−4.4)	
MBPT(2)/6-31G*	b	−13.8	−31.6
MBPT(2)/6-31G*	b	−13.0 (−7.6)	−29.8 (−26.1)
MBPT(2)/6-31G**	b	−12.5	
MBPT(2)/6-31++G*	c	−10.2 (−7.4)	−22.4 (−17.0)
MBPT(2)/6-311++G**	c	−8.7	−18.7 (−17.3)
MBPT(2)/6-311++G**	d	−8.7 (−6.4)	
SDQ-MBPT(4)/6-31G*	c	−11.6 (−7.6)	−26.6 (−23.3)
SDQ-MBPT(4)/6-31++G*	c	−9.1 (−6.3)	−20.2 (−14.8)
SDQ-MBPT(4)/6-311++G**	c	−7.8	−17.0
SDQ-MBPT(4)/6-311++G**	d	−7.9 (−5.6)	
MBPT(4)/6-311++G**	d	−8.6 (−6.1)	

[a] These include all thermal (translational, rotational, and vibrational) corrections. The thermal corrections were made by using, respectively, the MBPT(2)/6-31G** and SCF/6-31G* vibrational analyses for the 1:1 and 1:2 complexes. Some counterpoise corrected results are given in parentheses. [b] Calculated at the optimum geometry for the method. [c] Determined at the MBPT(2)/6-31G* optimum geometry. [d] Determined at the MBPT(2)/6-31G** optimum geometry.

Table VII. Comparison of Atomic Charges for the SCF/6-311++G** Method at the MBPT(2)/6-31G** Geometry for the 1:1 Complex and the MBPT(2)/6-31G* Geometry for the 1:2 Complex

atom	HF	H$_2$NOH	HF-H$_2$NOH	(HF)$_2$-H$_2$NOH
H[a]		0.25	0.29	0.32
N		−0.51	−0.68	−0.78
O		−0.28	−0.19	−0.19
H[b]		0.28	0.29	0.33
H[c]	0.30		0.36	0.46
F[c]	−0.30		−0.37	−0.42
H[d]				0.30
F[d]				−0.35

[a] The ammino hydrogen. [b] The hydroxyl hydrogen. [c] The atoms in the first HF molecule. [d] The atoms in the second HF molecule.

1:1 Complex (HF)H$_2$NOH. The most stable geometry was very similar to the cyclic structure proposed by Lascola and Andrews.[1] The MBPT(2)/6-31G** geometry is illustrated in Figure 1. With the primary attachment of the HF molecule to the nitrogen rather

Table VIII. Perturbations to the Vibrational Frequencies $\delta\omega = \omega(\text{complex}) - \omega(\text{monomer})$ of the HF and H$_2$NOH Moieties in the 1:1 and 1:2 Complexes[a]

Mode	(HF)H$_2$NOH	(HF)$_2$H$_2$NOH
H$_2$NOH torsion	100 (−8)	
OH stretch	−87 (−23)	−81
NO stretch	8 (−30)	−1
NH stretch (A′)	21	2
NH stretch (A″)	12	−5
NH$_2$ wag	29 (46)	59
NH$_2$ rock	−22	−8
NOH bend	104 (34)	90
H′F′ stretch	−664 (−920)	−708
H″F″ stretch		−246

[a] The experimental values are given in parentheses, and the frequencies shifts are in inverse centimeter units.

than the oxygen atom, a secondary hydrogen bond was permitted between the fluorine and the hydroxyl hydrogen. All methods gave qualitatively similar results. As with the monomers, most bond lengths were longer, bond angles smaller, and the atomic charges by the Mulliken definition larger for the second-order methods. They showed major differences only in the N–HF and F–HO hydrogen-bond distances. The MBPT(2)/6-31G** values for the two are 1.71 and 2.01 Å, respectively, close to the values of 1.7 and 2.1 Å proposed by Lascola and Andrews. The shorter than predicted secondary hydrogen-bond distance adds to the stability of the cyclic structure. The O–N–HF and N–H–F bond angles are 100.6 and 146.1° versus their proposed values of 90 and 160°. The ring appears to be somewhat more regular than anticipated.

At the optimized MBPT(2)/6-31G** geometry, the basis set was extended to the 6-31++G* and 6-31++G** sets and the method extended to the SDQ-MBPT(4) and the full MBPT(4) fourth-order methods. As detailed in Table VI, the association energy at the MBPT(4) level is −8.6 kcal/mol without the CP correction and −6.1 kcal/mol with the CP correction. The latter should be considered to be a conservative estimate since the CP correction normally overestimates the positive BSSE correction to the association energy.

The vibrational analysis is given in Table IV. For the lower frequency modes, the assignments were difficult to assign since the coupling between the various internal coordinates was strong. To evaluate the experimental assignments, the calculated and experimental perturbations to the monomer modes are listed in Table VIII. Although the harmonic frequencies give large errors as expected, the ordering of the vibrational modes and the perturbations show good qualitative agreement. The MBPT(2) harmonic frequencies have errors that are larger than the 5% values commonly observed for small isolated molecules.[23] This is particularly true for the torsional, librational, NOH bending and HF stretching modes, which couple significantly with the hydrogen bonds. This coupling may introduce a strong anharmonicity into these modes. Such errors in the MBPT(2) harmonic frequencies have been observed before.[24] The calculated NOH torsional mode at 507 cm⁻¹ appears to not support Lascola and Andrew's suspicion that it might be identified with the observed 368 cm⁻¹ frequency. The two values show perturbations of opposite sign. Specific sets of the internal coordinates showed considerable mixing. The HF symmetric libration at 885 cm⁻¹, NH$_2$ wag at 1163 cm⁻¹, and the NO stretch at 865 cm⁻¹ exhibited considerable mixing and made these assignments approximate at best. Such mode mixing was used to explain the anomalous shifts to the NO stretch obtained upon isotopic substitution. The HF and OH stretching modes showed the expected red shift for bonds including hydrogen-bonded atoms, and the NOH bend showed the expected blue shift.

1:2 Complex (HF)$_2$H$_2$NOH. Considerably less experimental information is available on the 1:2 complex. The strong mode

(24) Szczesniak, M. M.; Kurnig, I. J.; Scheiner, S. *J. Chem. Phys.* **1980**, *89* (5), 3131.

mixing in the FTIR spectra made the mode assignment particularly difficult. Table III contains the results of the geometry optimizations, while Table IV gives the harmonic vibrational analysis.

Again, the most stable geometry among the several options explored was the ring structure proposed by Lascola and Andrews where both HF monomers link to form the seven-member ring sequence $-F'-H'-N-O-H-F''-H''-$. The MBPT(2)/6-31G* geometry is given in Figure 2. The distance between the second fluorine and the hydroxyl hydrogen is now much shorter, giving three strong hydrogen bonds versus one strong and one weak bond in the 1:1 complex. As a result, the association enthalpy of the 1:2 complex is almost 3 times larger as documented in Table VI. These results give an association enthalpy of about -17 to -19 kcal/mol at the MBPT(2) or SDQ-MBPT(4) levels for this complex. With use of the MBPT(2)/6-31G* results, the N–HF and F–HO distances in the 1:2 complex have values of 1.57 and 1.78 Å, which are appreciably shorter than those of 1.71 and 2.01 Å in the 1:1 complex. Additionally, the HF–HF bond distance in the 1:2 complex is only 1.56 Å, much shorter than that of 1.68 Å found in the dimer $(HF)_2$ at the MBPT(2)/6-31G* level. The ring structure is much tighter than expected.

As observed by Lascola and Andrews, the vibrational mode mixing was considerable, making the assignments of the modes in Table IV very crude at best except for the higher frequency modes. Due to computing constraints, the vibrational analysis of the trimer was completed at the SCF/6-31G* level of theory rather than the MBPT(2)/6-31G** level used for the dimer. However, as the data in Table IV indicate, the two levels gave similar results for the dimer. Only twice, when there was significant mode mixing, were two frequencies interchanged. The intensities compared favorably, and both methods gave the same signs for the perturbations to the frequencies of the monomers, i.e., $\omega(\text{dimer}) - \omega(\text{monomer})$. For the trimer, the qualitative perturbations to the vibrational modes, as elaborated in Table VIII, were what would be expected from the effects of hydrogen bonding.

Conclusions

These results substantiate many of the conclusions derived from the FTIR spectra of the $(HF)_nH_2NOH$ clusters. The 1:2 complex however exhibited tighter than expected bonding. For the 1:1 and 1:2 complexes, the association energies are approximately -6 to -9 and -17 to -19 kcal/mol, respectively. Most of the assumptions made in the vibrational assignments for the 1:1 complex appear to be valid.

A Copper(II) Bromide Dimer System Exhibiting Piezochromic and Thermochromic Properties: The Crystal Structure and Electronic Spectroscopy of the Two Room-Temperature Phases of Bis(tetrapropylammonium) Hexabromodicuprate(II)

Brian Scott and Roger D. Willett*

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99164-4630. Received October 9, 1990

Abstract: Two phases of the compound bis(tetrapropylammonium) hexabromodicuprate(II) were synthesized and their crystal structures determined. The orange phase exhibits piezochromism, with the application of a small force causing it to spontaneously transform to the green phase. The green phase is thermochromic and transforms to the orange phase upon heating to 90 °C. The green triclinic phase, with space group $P\bar{1}$, $a = 9.612$ (2) Å, $b = 9.602$ (2) Å, $c = 12.006$ (3) Å, $\alpha = 102.27$ (2)°, $\beta = 104.30$ (2)°, $\gamma = 112.79$ (1)°, $V = 929.2$ (3) Å³, $Z = 1$, $d_x = 1.75$ g/cm³, and $R = 0.0642$, is stable at room temperature. The orange phase, metastable at room temperature, is monoclinic with space group $C2/c$, $a = 17.460$ (6) Å, $b = 14.625$ (4) Å, $c = 15.061$ (4) Å, $\beta = 103.82$ (2)°, $V = 3735$ (2) Å³, $Z = 4$, $d_x = 1.74$ g/cm³, and $R = 0.0839$. Both phases have isolated $Cu_2Br_6{}^{2-}$ dimers with very similar geometries. The correlation of polarized absorption spectral data and X-ray crystallography show that the difference in orientation of the $Cu_2Br_6{}^{2-}$ chromophores in the two phases is responsible for the color variance. A prominent feature of the visible absorption spectra is the presence of a so-called "dimer" transition at approximately 13 000 cm⁻¹. This assignment gives strong support for ligand to metal character of the dimer transition, and not a simultaneous excitation of d–d transitions on both copper centers. EHMO calculations support this assignment.

Introduction

The compound to be described in this work has many interesting features. First, it is a thermochromic compound in which high- and low-temperature phases coexist at room temperature. This is not itself unknown,[1] but the fact that the high-temperature phase is metastable—a small stress to the crystal causes it to spontaneously transform to the low-temperature phase—is unusual. Second, the color difference between the two phases is not the result of a change in coordination geometry or ligand field strength, as is commonly observed in copper halide materials. The majority of these materials consist of networks of $CuCl_4{}^{2-}$ anions linked to ammonium groups on the cations via hydrogen bonding. The change in coordination geometry, from square planar to tetrahedral, is caused by weakening of this hydrogen-bonding network, brought on by increased thermal motion in the cations as the temperature is raised.[2] In the only thermochromic dimer systems, $[(CH_3)_2CHNH_3]_2Cu_2X_6$ with X = Cl or Br, a striking change

---

(1) Battaglia, L. P.; Bonamartini-Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1982**, *21*, 3919.

(2) Bloomquist, D. R.; Willett, R. D. *Coord. Chem. Rev.* **1982**, *47*, 125.