Ab Initio Characterization of the Structure, Vibrational, and Energetic Properties of $Br^-\cdot HOCl$, $Cl^-\cdot HOBr$, and $Br^-\cdot HOBr$ Anionic Complexes

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Ab initio molecular orbital methods have been employed to determine molecular structure, vibrational frequencies, and relative energetics of $Br^-\cdot HOCl$, $Cl^-\cdot HOBr$, and $Br^-\cdot HOBr$ anionic complexes. These parameters were determined using second-order Møller−Plesset perturbation theory (MP2) and coupled cluster methods. The minimum energy structures for all three complexes are reported. The minima for the mixed halogen conformers place the halogen anion in complexation through the hydrogen. The calculated binding energies are 23.3, 19.5, and 19.5 kcal mol^{-1} for $Cl^-\cdot HOBr$, $Br^-\cdot HOCl$, and $Br^-\cdot HOBr$, respectively.

I. Introduction

Heterogeneous reactions on the surface of polar stratospheric clouds (PSCs) are believed to be a primary means for activation of bromine and chlorine radicals during the polar spring. Hypochlorous acid, HOCl, which is present in trace amounts in the stratosphere, is produced by the hydrolysis of chlorine nitrate ($ClONO_2$) on the surface of PSCs during the polar winter by the following reaction:[1−3]

$$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(s) \quad (1)$$

Reaction 1 produces HOCl very rapidly, thus contributing to the springtime development of the Antarctic ozone "hole". Hypobromous acid, HOBr, is also present in trace concentrations in the stratosphere. It is also formed in a similar manner on the surface of PSCs during the dark polar winter.[4,5]

$$BrONO_2(g) + H_2O(s) \rightarrow HOBr(g) + HNO_3(s) \quad (2)$$

Experimental groups have explained the consequent loss of ozone in the polar spring to a continued reaction of the HOCl and HOBr formed in reactions 1 and 2, with HCl and HBr species present in PSCs. The kinetics and reactive uptake of these reactions have been thoroughly examined.[6−11] Important heterogeneous processes that involve HOCl and HOBr are given below. Each reaction converts a stable halogen reservoir species into the photochemically active form of the halogen. These reactions have been found to involve bromine and chlorine in the same reaction, as well as reactions involving only chlorinated and brominated species.

$$HOCl(g) + HCl(s) \rightarrow Cl_2(g) + H_2O(s) \quad (3)$$

While it is accepted that this type of reactivity takes place on

$$HOCl(g) + HBr(s) \rightarrow BrCl(g) + H_2O(s) \quad (4)$$

$$HOBr(g) + HCl(s) \rightarrow BrCl(g) + H_2O(s) \quad (5)$$

$$HOBr(g) + HBr(s) \rightarrow Br_2(g) + H_2O(s) \quad (6)$$

PSCs, the mechanism of this reaction remains to be determined. The presence of Cl^- on PSCs is known to catalyze the conversion of $ClONO_2$ to photochemically active Cl_2.[12−14] Theoretical studies have indicated that the presence of Cl^- could have a similar impact on the conversion of HOCl to Cl_2.[15,16] Eigen and Kustin[17] have proposed a general mechanism for this conversion. Using reaction 3, an example is shown below:

$$HOCl + Cl^- \rightarrow [HOCl]Cl^- \quad (7)$$

Chu and Chu[11] have suggested an analogous mechanism for

$$[HOCl]Cl^- + H^+ \rightarrow Cl_2 + H_2O \quad (8)$$

the heterogeneous reaction of HOCl + HBr → BrCl + H_2O, shown below.

$$HOCl + Br^- \rightarrow [HOCl]Br^- \quad (9)$$

In an effort to further elucidate this important reactivity, we

$$[HOCl]Br^- + H^+ \rightarrow BrCl + H_2O \quad (10)$$

report ab initio calculations pertaining to the structure, vibrational frequencies, and relative energetics of complexes similar to those in reactions 7−9. We seek to determine the binding location of the halogen anion to the acid and whether the anion prefers to attach to the hydrogen or the halogen in the acid. Where possible, we have included comparison data from experiments. Also, to serve as another point of comparison, we have included calculations and data from $Cl^-\cdot H_2O$ and $Br^-\cdot H_2O$ complexes.

II. Calculation Method

Ab initio molecular orbital calculations were performed using the GAUSSIAN 94 package of programs.[18] All geometries were fully optimized using second-order Møller−Plesset perturbation theory (MP2)[19] and coupled cluster theory using single and double excitation, along with a perturbational estimation of triplet excitation [CCSD(T)].[20] The optimizations are performed using one basis set of double-ζ quality, 6-31G(d), and two basis sets of triple-ζ quality, 6-311G(d,p) and 6-311++G(2df,2p). Vibrational frequencies were computed numerically with a 6-311G(d,p) basis set at the CCSD(T) level of theory.

III. Results and Discussion

A. Calibration Calculations $Cl^-\cdot H_2O$ and $Br^-\cdot H_2O$. To our knowledge, there have been no previous studies on the

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TABLE 1: Geometries[a] at Various Levels of Theory for $Cl^-\cdot H_2O$ and $Br^-\cdot H_2O$ Anion Cluster

		geometric parameters				
species	level of theory	r(H′O)	r(OH)	r(H′X)	θ(XHO)	θ(HOH)
$Cl^-\cdot H_2O$	MP2/6-31G(d)	0.989	0.968	2.227	160.9	99.4
	MP2/6-311G(d,p)	0.976	0.958	2.219	159.7	98.2
	MP2/6-311++G(2df,2p)	0.988	0.957	2.102	168.7	100.9
	CCSD(T)/6-31G(d)	0.988	0.971	2.249	160.4	99.4
	CCSD(T)/6-311G(d,p)	0.975	0.959	2.233	159.9	98.3
	CCSD(T)/6-311++G(2df,2p)	0.985	0.958	2.132	167.7	100.9
$Br^-\cdot H_2O$	MP2/6-31G(d)	0.986	0.969	2.403	156.5	99.1
	MP2/6-311G(d,p)	0.971	0.958	2.432	154.6	97.9
	MP2/6-311++G(2df,2p)	0.980	0.957	2.324	165.9	100.9
	CCSD(T)/6-31G(d)	0.986	0.971	2.434	155.2	99.0
	CCSD(T)/6-311G(d,p)	0.971	0.959	2.450	154.0	98.0
	CCSD(T)/6-311++G(2df,2p)	0.979	0.959	2.367	164.3	100.8

[a] All bond distances are reported in angstroms and bond angles in degrees.

TABLE 2: Vibrational Frequencies (cm^{-1}) for $Cl^-\cdot H_2O$ and $Br^-\cdot H_2O$ Anion Cluster[a]

species	mode no.	mode symmetry	mode description	CCSD(T)/6-311G(d,p)	exp
$Cl^-\cdot H_2O$	1	a′	HO stretch, uncomplexed	3785	3698[b]
	2		HO stretch, complexed	3524	3285[b], 3103[c]
	3		HOH bend	1806	
	4		H_2O in−plane rock	325	
	5		Cl−H′ stretch	191	
	6	a″	H bonded to the ion	736	
$Br^-\cdot H_2O$	1	a′	HO stretch, uncomplexed	3945	
	2		HO stretch, complexed	3565	3368[d]
	3		HOH bend	1736	
	4		H_2O in−plane rock	368	
	5		Br−H' stretch	169	
	6	a″	H bonded to the ion	700	

[a] Experimental frequencies for H_2O: 3943, 3832, 1648 cm^{-1}. [b] Reference 18 [c] Reference 21. [d] Ayotte, P.; et al. *J. Phys. Chem.* **1998**, *102*, 3067.

anionic $Br^-\cdot HOCl$ or $Cl^-\cdot HOBr$ systems. Thus, to calibrate our calculations, we have performed geometry optimization and harmonic frequency calculations on $Cl^-\cdot H_2O$ and $Br^-\cdot H_2O$ anionic complexes, for which there are numerous theoretical and experimental studies.

Molecular geometries have been fully optimized at all levels of theory. Our best estimate of the equilibrium geometry for $Cl^-\cdot H_2O$ is at the CCSD(T)/6-311++G(2df,2p) level. Our results are in good agreement with previous ab initio efforts. For instance, we report a Cl−H′ bond length of 2.132 Å at the CCSD(T)/6-311++G(2df,2p) level. This corresponds well to the 2.151 Å value reported by Choi et al.[18] at the MP2/6-311++G** level. Also, this value is in agreement with the 2.115 Å value determined by Combariza et al.[19] using density functional methods. For the H′O bond, Combariza and Kestner[19] report a value of 0.96 Å. This is in excellent agreement with our result of 0.958 Å at the CCSD(T)/6-311++G(2df,2p) level. Our best estimation of the H′OH angle is 100.9°. Combariza et al.[19] report a similar value of 102.3° from their density functional study, and our value is also in agreement with 100.6° reported by Xantheas[20] with an MP4/aug-cc-pVTZ basis set. The complete results from these calculations are provided in Table 1.

We report harmonic vibrational frequencies for $Cl^-\cdot H_2O$ in Table 2. These frequencies were calculated for the C_s minimum energy conformation. All frequencies are predicted to be positive, real numbers, which indicate that the C_s structure is truly a minimum energy structure on the $Cl^-\cdot H_2O$ potential energy surface. For $Cl^-\cdot H_2O$, we report six normal vibrational modes. The modes ν_1 and ν_2 are the uncomplexed and complexed OH stretches, respectively. The ν_3 mode corresponds to the HOH bending frequency, and ν_4 is the HOH in-plane rocking motion. The fifth and sixth modes (ν_5 and ν_6) correspond to the chlorine anion bonded to H′, and to the out-of-plane motion of the H′ bonded to the ion, respectively. For $Cl^-\cdot H_2O$, we see the uncomplexed OH stretch occurring at 3785 cm^{-1}. This value is in excellent agreement with 3698 cm^{-1}, reported by Choi et al.[18] Also, our calculated OH complexed stretch is predicted to occur at 3524 cm^{-1}. This compares with the experimental value of 3285 cm^{-1} for the complexed OH stretch[18] and the experimental value of 3103 cm^{-1} from argon predissociation spectroscopy stretches.[21]

TABLE 3: Relative Energetics for $Cl^-\cdot H_2O$ and $Br^-\cdot H_2O$ Anion Cluster[a]

species	level of theory	$X^-\cdot H_2O \rightarrow X^- + H_2O$
$Cl^-\cdot H_2O$	MP2/6-31G(d)	15.4
	MP2/6-311G(d,p)	12.9
	MP2/6-311++G(2df,2p)	14.4
	CCSD(T)/6-31G(d)	15.0
	CCSD(T)/6-311G(d,p)	12.7
	CCSD(T)/6-311++G(2df,2p)	14.1
$Br^-\cdot H_2O$	MP2/6-31G(d)	15.9
	MP2/6-311G(d,p)	12.3
	MP2/6-311++G(2df,2p)	12.0
	CCSD(T)/6-31G(d)	15.3
	CCSD(T)/6-311G(d,p)	12.0
	CCSD(T)/6-311++G(2df,2p)	11.5

[a] Relative energies are reported in kcal mol^{-1}.

The relative energies for $Cl^-\cdot H_2O$ are included in Table 3. Again, our best estimate of the binding energy of this complex is determined at the CCSD(T)/6-311++G(2df,2p) level of theory. At this level of theory, we find the complex to be bound by 14.1 kcal mol^{-1}. This value compares very well with the previously calculated values of 13.61 kcal mol^{-1}, as well as 12.9 and 17.2 kcal mol^{-1}.[22,23] When compared with experimental results,[24,25] our value of 14.1 kcal mol^{-1} is in excellent agreement with the experimental determinations of 14.3 and 14.8 kcal mol^{-1}. This indicates that our computational method

provides reasonable and reliable results. Moreover, they are good systems for calibrating the calculations on $Cl^-\cdot HOBr$ and $Br^-\cdot HOCl$ species for which no experimental results are available.

For $Br^-\cdot H_2O$, we also report the fully optimized molecular geometries in Table 1. Again, we have used the C_s structure, which is of minimum energy. Our best estimation for the equilibrium geometry parameters occurs again at the CCSD(T)/6-311++G(2df,2p) level of theory. We note that all parameters have converged to this level. At this level, we report an X−H−O angle of 164.3°. This value agrees well with the 165° value reported by Xantheas,[20] using MP2/MP4(aug-cc-pVDZ/aug-cc-pVTZ) basis sets. Also, our calculated value for the H′O bond only differs by 0.006 Å when compared to Xantheas' result. We note here, as well, similar trends in shortening the H′O bond. We observe the H′O bond in Cl^-H_2O to be 0.985 Å, and the H′O bond for $Br^-\cdot H_2O$ to be 0.979 Å, both at the CCSD(T)/6-311++G(2df,2p) level of theory. Xantheas[20] noted a similar trend with MP2/MP4(aug-cc-pVDZ/aug-cc-pVTZ) calculations (H′O = 0.992 and 0.987 Å for $Cl^-\cdot H_2O$ and $Br^-\cdot H_2O$, respectively).

The harmonic vibrational frequencies for $Br^-\cdot H_2O$ have been calculated and are shown in Table 2. Again, we see six normal vibrational modes. These normal modes are represented by ν_1 and ν_2 for uncomplexed (OH) and complexed (H′O) stretches, respectively. The H′OH bend is ν_3, while the H_2O in-plane rock with respect to Br^- is represented by ν_4. ν_5 is the van der Waals stretch motion for the Br−H′, and ν_6 is the out-of-plane motion of the hydrogen bonded to the Br^-. We note that all frequencies presented have real, positive values, which indicates that the structure is a true minimum on the potential energy surface. We report frequencies at the CCSD(T)/6-311G(d,p) level. At this level of computation, we find the uncomplexed OH stretch (ν_1) to occur at 3945 cm^{-1}. We see good agreement between the calculated and experimental[26] frequency for the OH stretch occurring in H_2O at 3943 cm^{-1}. Also, the complexed H′O stretch is estimated to occur at 3565 cm^{-1}. This is in good agreement with experimentally determined vibrational frequencies established by Ayotte et al.[27] They report a complexed H′O stretch occurring in $Br^-\cdot H_2O$ at 3368 ± 3 cm^{-1}.

We have also calculated the relative binding energies for $Br^-\cdot H_2O$. These results are included in Table 3. The binding energy has converged to give our best estimation at the CCSD(T)/6-311++G(2df,2p) level. Here we predict that the $Br^-\cdot H_2O$ complex is bound by 11.5 kcal mol^{-1}. This is in excellent agreement with the experimental[26] value of 12.3 kcal mol^{-1}.

B. $Cl^-\cdot$HOBr vs $Cl^-\cdot$BrOH. A primary goal of this study is to determine the equilibrium geometry of the chlorine anion as it binds to hypobromous acid (HOBr). To accomplish this, we have used two possible conformers of the complex. The first form places the chlorine anion in complexation through the hydrogen of HOBr. The second conformer considered places the chlorine anion in complexation through the bromine of HOBr. The geometries are given in Table 4. In the first conformation, $Cl^-\cdot HOBr$, we see interesting effects when compared to the geometry of $Cl^-\cdot H_2O$, primarily the shortening of the Cl−H′ bond. This length decreases by 0.22 Å relative to $Cl^-\cdot H_2O$, indicating that the chlorine is more strongly bound to HOBr than to H_2O. Also, there is a relatively small lengthening of the H′O bond in $Cl^-\cdot HOBr$ relative to uncomplexed HOBr. This bond length has increased by 0.052 Å, which indicates that the chlorine complexation has little effect on the bonds in HOBr. This is further evidenced when examining the HOBr angle in $Cl^-\cdot HOBr$ relative to uncomplexed HOBr. At the CCSD(T)/6-311++G(2df,2p) level, the HOBr angle only changes by 1° upon chlorine complexation.

For the other conformation, $Cl^-\cdot BrOH$, we see subtle effects due to chlorine complexation through the bromine of HOBr. First we note that, at the CCSD(T)/6-311++G(2df,2p) level, the HOBr angle in $Cl^-\cdot BrOH$ closes by 2.8° relative to uncomplexed HOBr and by 3.8° relative to $Cl^-\cdot HOBr$. This results in a closer arrangement of the atoms in the complex. However, when comparing the geometry of HOBr and $Cl^-\cdot HOBr$, one observes a small HOBr geometry distortion after chlorine complexation. In uncomplexed HOBr at the CCSD(T)/6-31++G(2df,2p) level, we see an OH bond length of 0.964 Å and a BrO bond length of 1.84 Å. In $Cl^-\cdot HOBr$ at the CCSD(T)/6-311++G(2df,2p) level, we see an OH bond length of 0.962 Å and a BrO bond length of 1.982 Å. Thus, the BrO bond in $Cl^-\cdot BrOH$ is only 0.143 Å longer than in HOBr.

The vibrational frequencies for both $Cl^-\cdot HOBr$ and $Cl^-\cdot BrOH$ are included in Table 5. We report all frequencies are positive real numbers, which indicates that the geometry is a true minimum structure on the potential energy surface. For the OH stretch in $Cl^-\cdot HOBr$, we report a value of 3026 cm^{-1}. This corresponds well to the HO stretch occurring in isolated HOBr, at 3838 cm^{-1} (experimental[28] 3590 cm^{-1}). This red shift of 812 cm^{-1} is reasonable when inspecting the HO bond length in HOBr and $Cl^-\cdot HOBr$. At the CCSD(T)/6-311++G(2df,2p) level, we calculate an HO bond length of 0.964 Å, while in $Cl^-\cdot HOBr$, the HO bond length was calculated to be 1.016 Å. The longer HO bond suggests that the frequency of this motion should be red shifted. Also, the HO stretch in $Cl^-\cdot HOBr$ is in agreement with the complexed HO stretch in $Cl^-\cdot H_2O$. Our CCSD(T) result is close to the 3285 cm^{-1} reported by Choi et al.[18] Upon further inspection, we see the HO bond length in $Cl^-\cdot H_2O$ to be 0.985 Å at the CCSD(T)/6-311++G(2df,2p) level. This value is 0.031 Å shorter than our calculation for the HO bond in $Cl^-\cdot HOBr$. Thus, we see that, as the calculated HO bond length increases through the series HOBr, $Cl^-\cdot H_2O$, and $Cl^-\cdot HOBr$, the HO stretching frequency decreases through the same series. The HOBr bending mode is also affected by the chlorine complexation. We noted previously that chlorine complexation through the hydrogen affected the geometry of the HOBr monomer. This effect is also seen in the HOBr bending frequency. The lengthening of the HO bond by 0.052 Å, as well as the closing of the HOBr angle by 1° (both of which are results of the Cl^- complexation), causes the HOBr bending frequency to be blue shifted. Also, the BrO stretching frequency in $Cl^-\cdot HOBr$ is in good agreement with the experimental BrO stretching frequency from HOBr. We estimate a BrO stretch to occur in $Cl^-\cdot HOBr$ at 575 cm^{-1}, which is relatively similar to the experimental BrO stretch of 626 cm^{-1}.[28] We also predict the Cl^--H stretch to occur at 259 cm^{-1}.

For $Cl^-\cdot BrOH$, from our CCSD(T)/6-311G(d,p) calculations in Table 5, we report an OH stretching frequency of 3822 cm^{-1}. This is red shifted by 16 cm^{-1} from the OH stretch. Here, we see that the Cl^- complexation has little effect on the HOBr bending frequency. We calculate an HOBr bending frequency of 1016 cm^{-1}, which is in excellent agreement with the calculated and experimental HOBr bend[21] of 1164 cm^{-1}. The largest difference in bond lengths in $Cl^-\cdot BrOH$ relative to HOBr is the elongation of the BrO bond. In HOBr, we report a BrO bond length of 1.84 Å, while in $Cl^-\cdot BrOH$, we report a BrO bond length of 1.98 Å. This effect is also seen in the BrO stretching frequency, namely the BrO stretch, which decreases from 575 cm^{-1} (HOBr) to 435 cm^{-1} ($Cl^-\cdot BrOH$). The elonga-

TABLE 4: Geometries[a] for $Cl^-\cdot HOBr$, $Cl^-\cdot BrOH$, $Br^-\cdot HOCl$, $Br^-\cdot ClOH$, $Br^-\cdot HOBr$, and $Br^-\cdot BrOH$

		geometric parameters				
species	level of theory	*r*(Cl-X)	*r*(OH)	*r*(BrO)	θ(Cl-XO)	θ(HOBr)
$Cl^-\cdot HOBr$	MP2/6-31G(d)	1.951	1.027	1.849	175.9	102.3
X = H	MP2/6-311G(d,p)	1.914	1.013	1.844	176.1	102.7
	MP2/6-311++G(2df,2p)	1.864	1.026	1.804	176.6	103.8
	CCSD(T)/6-31G(d)	1.980	1.022	1.873	175.6	102.1
	CCSD(T)/6-311G(d,p)	1.939	1.008	1.868	175.5	102.5
	CCSD(T)/6-311++G(2df,2p)	1.912	1.016	1.824	176.2	103.9
$Cl^-\cdot BrOH$	MP2/6-31G(d)	2.603	0.980	1.994	179.6	102.2
X = Br	MP2/6-311G(d,p)	2.660	0.962	1.980	179.1	97.8
	MP2/6-311++G(2df,2p)	2.516	0.963	1.991	179.6	99.2
	CCSD(T)/6-31G(d)	2.647	0.976	2.003	179.5	98.5
	CCSD(T)/6-311G(d,p)	2.713	0.962	1.982	179.0	98.6
	CCSD(T)/6-311++G(2df,2p)	2.582	0.962	1.983	179.7	100.1

		geometric parameters				
species	level of theory	*r*(Br-X)	*r*(OH)	*r*(ClO)	θ(Br-XO)	θ(HOCl)
$Br^-\cdot HOCl$	MP2/6-31G(d)	2.134	1.019	1.797	178.0	103.1
X = H	MP2/6-311G(d,p)	2.110	1.003	1.710	176.5	102.9
	MP2/6-311++G(2df,2p)	2.079	1.010	1.680	176.3	103.6
	CCSD(T)/6-31G(d)	2.170	1.015	1.730	177.1	102.8
	CCSD(T)/6-311G(d,p)	2.138	1.000	1.735	175.4	102.5
	CCSD(T)/6-311++G(2df,2p)	2.130	1.004	1.699	175.2	103.5
$Br^-\cdot ClOH$	MP2/6-31G(d)	2.768	0.976	1.831	178	99.2
X = Br	MP2/6-311G(d,p)	2.792	0.963	1.840	178.6	98.1
	MP2/6-311++G(2df,2p)	2.576	0.964	1.876	180.0	97.6
	CCSD(T)/6-31G(d)	2.844	0.977	1.830	178.5	99.8
	CCSD(T)/6-311G(d,p)	2.901	0.962	1.831	178.0	98.9
	CCSD(T)/6-311++G(2df,2p)	2.725	0.962	1.833	179.6	99.2

		geometric parameters				
species	level of theory	*r*(Br-X)	*r*(OH)	*r*(BrO)	θ(Br-XO)	θ(HOBr)
$Br^-\cdot HOBr$	MP2/6-31G(d)	2.115	1.021	1.850	180.0	101.6
X = H	MP2/6-311G(d,p)	2.115	1.003	1.846	176.6	102.3
	MP2/6-311++G(2df,2p)	2.074	0.963	1.991	176.8	98.9
	CCSD(T)/6-31G(d)	2.155	1.016	1.874	179.0	101.6
	CCSD(T)/6-311G(d,p)	2.151	0.998	1.869	175.8	102.1
	CCSD(T)/6-311++G(2df2p)	2.127	1.004	1.827	176.3	103.6
$Br^-\cdot BrOH$	MP2/6-31G(d)	2.711	0.976	2.001	179.5	97.8
X = Br	MP2/6-311G(d,p)	2.775	0.963	1.992	179.1	97.3
	MP2/6-311++G(2df,2p)	2.680	0.964	1.991	179.7	98.9
	CCSD(T)/6-31G(d)	2.755	0.977	2.012	179.4	98.3
	CCSD(T)/6-311G(d,p)	2.838	0.962	1.993	178.9	98.3
	CCSD(T)/6-311++G(2df,2p)	2.706	0.962	1.977	179.8	100.0

[a] All bond distances are reported in angstroms and bond angles in degrees.

tion of the BrO bond by 0.14 Å induces a BrO stretching red shift of 140 cm^{-1}.

The total energies for $Cl^-\cdot HOBr$ and $Cl^-\cdot BrOH$ anionic clusters are given in Table 6. In Table 7, we report the zero-point energy corrected binding energies of the complexes, as well as the relative energies between $Cl^-\cdot HOBr$ and $Cl^-\cdot BrOH$. We find the $Cl^-\cdot HOBr$ structure to be the lowest in energy. At the CCSD(T)/6-311++G(2df,2p) level, we calculate $Cl^-\cdot HOBr$ to be lower in energy by 1.5 kcal mol^{-1}. We also estimate the binding energies of both complexes. We find the $Cl^-\cdot HOBr$ complex to be bound by 23.0 kcal mol^{-1} and $Cl^-\cdot BrOH$ to be bound by 21.5 kcal mol^{-1}. These energetic calculations suggest that, if the heterogeneous reaction mechanism proposed by Chu and Chu[11] exists, the Cl^-[HOBr] intermediate is likely to be of the form $Cl^-\cdot HOBr$.

C. $Br^-\cdot HOCl$ vs $Br^-\cdot ClOH$. Like the $Cl^-\cdot HOBr$ system, the $Br^-\cdot HOCl$ system has two conformers. The first conformer takes the form of the bromine anion complexing to the HOCl through the hydrogen, whereas in the second conformation, the bromine anion is in complexation through the chlorine of HOCl. A complete list of fully optimized geometrical parameters for both conformations comprises Table 4. For the first conformation of Br^- bound through the hydrogen, a comparison with previous calibration calculations for the $Br^-\cdot H_2O$ system yields some interesting results. We first note that there is a significant shortening of the Br^-—H bond in $Br^-\cdot H_2O$. This bond length was further reduced by 0.237 Å, indicating that the Br^-—H bond in $Br^-\cdot HOCl$ is stronger than that in $Br^-\cdot H_2O$. Also, the Br^-—HO angle in $Br^-\cdot HOCl$ increases by 10.9° relative to $Br^-\cdot H_2O$. This result also indicates that the Br^- is more tightly bound in $Br^-\cdot HOCl$ than in $Br^-\cdot H_2O$. We see that the HO bond length in $Br^-\cdot HOCl$ is 0.015 Å longer than for HOCl, indicating that the bromine complexation exhibits a marginal effect on the HO bonding.

For the $Br^-\cdot ClOH$ conformer, we see the most effect on the HOCl angle. At the CCSD(T)/6-311++G(2df,2p) level, the HOCl angle in HOCl is 102.4°. However, in $Br^-\cdot ClOH$, the angle closes to 99.2°. From this, we see that, in this conformation, the ClOH geometry is more constrained in $Br^-\cdot ClOH$ than for HOCl. Also, the ClO bond is affected by the bromine complexation. In HOCl, we calculate a ClO bond length of 1.707 Å. This ClO distance increases upon bromine complexation through chlorine to 1.833 Å. These factors indicate that the

TABLE 5: Vibrational Frequencies (in cm^{-1}) for Cl$^-$·HOBr, Cl$^-$·BrOH, Br$^-$·HOCl, Br$^-$·ClOH, Br$^-$·HOBr, and Br$^-$·BrOH Anion Clusters[a]

species	mode no.	mode symmetry	mode description	CCSD(T)/6-311G(d,p)
HOCl	1	a′	HO stretch	3840
	2		HOCl bend	1219
	3		ClO stretch	664
HOBr	1	a′	HO stretch	3838
	2		HOBr bend	1164
	3		BrO stretch	575
Cl$^-$·HOBr	1	a′	HO stretch	3026
	2		HOBr bend	1408
	3		BrO stretch	829
	4		Cl−H' stretch	574
	5		HOBr in-plane rock	259
	6	a″	out-of-plane motion of H bonded to the ion	88
Cl$^-$·BrOH	1	a′	HO stretch	3822
	2		HOBr bend	1016
	3		BrO stretch	435
	4		Cl−Br stretch	165
	5		HOBr in-plane rock	157
	6	a″	out-of-plane motion of Cl ion bonded to BrOH	150
Br$^-$·HOCl	1	a′	HO stretch	3184
	2		HOCl bend	1405
	3		ClO stretch	659
	4		Br^{--}-H stretch	747
	5		HOCl in-plane rock	216
	6	a″	out-of-plane motion of the H bonded to the ion	83
Br$^-$·ClOH	1	a′	HO stretch	3848
	2		HOCl bend	1094
	3		ClO stretch	479
	4		HOCl in-plane rock	144
	5		Br^{--}-Cl stretch	105
	6	a″	out-of-plane motion of the H bonded to the ion	158
Br$^-$·HOBr	1	a′	HO stretch	3202
	2		HOBr bend	1361
	3		BrO stretch	731
	4		Br−H′ stretch	575
	5		HOBr in-plane rock	208
	6	a″	out-of-plane motion of the H bonded to the ion	64
Br$^-$·BrOH	1	a'	HO stretch	3845
	2		HOBr bend	1016
	3		BrO stretch	439
	4		Br−Br′ stretch	144
	5		HOBr in-plane rock	135
	6	a″	out-of-plane motion of the H bonded to the ion	123

[a] Experimental frequencies for HOBr: 3590, 1164, and 626 cm^{-1}. Experimental frequencies for HOCl: 3581, 1239, and 718 cm^{-1}, taken from ref 26. Experimental frequencies for HOBr: 3590, 1164, and 626 cm^{-1}, taken from ref 26.

TABLE 6: Total Energies for Anion Clusters and Monomers[a]

level of theory	Cl$^-$·HOBr	Cl$^-$·BrOH	HOBr	Cl$^-$	Br$^-$·HOCl	Br$^-$·ClOH	HOCl	Br$^-$	Br$^-$·HOBr	Br$^-$·BrOH
MP2/6-31G(d)	−3105.29210	−3105.28813	−2645.58910	−459.66182	−3105.28904	−3105.27155	−535.16944	−2570.07908	−5215.70922	−5215.70956
MP2/6-311G(d,p)	−3108.29790	−3108.29025	−2648.51368	−459.74884	−3108.29122	−3108.27443	−535.30317	−2572.95404	−5221.50046	−5221.49653
MP2/6-311++G(2df,2p)	−3108.48682	−3108.48366	−2648.62514	−459.82115	−3108.48216	−3108.46861	−535.42487	−2573.02273	−5221.68220	−5221.68077
CCSD(T)/6-31G(d)	−3105.28860	−3105.28366	−2645.58212	−459.66654	−3105.28606	−3105.26777	−535.18356	−2570.06349	−5215.68481	−5215.68335
CCSD(T)/6-311G(d,p)	−3107.87540	−3107.86697	−2648.12635	−459.71447	−3107.86878	−3107.85116	−535.26337	−2572.57231	−5220.73024	−5220.72500
CCSD(T)/6-311++G(2df,2p)	−3108.03977	−3108.03458	−2648.21882	−459.78220	−3108.03610	−3108.02001	−535.37775	−2572.62575	−5220.87690	−5220.87297

[a] Total energies are in Hartrees.

bromine through chlorine complexation distorts HOCl more than does bromine through hydrogen complexation.

We report the harmonic vibrational frequencies for both conformers in Table 5. Many of the structural charges noted above are manifested in the shifts in the vibrational frequencies compared to the HOCl monomer. From comparison with the vibrational modes of HOCl, we see there are significant frequency shifts due to bromine complexation. At the CCSD(T)/6-311G(d,p) level, we calculate the HO stretch in Br$^-$·HOCl to occur at 3184 cm^{-1}. This is red shifted by 656 cm^{-1} from the HO stretch in HOCl[28] (3840 cm^{-1}). The red shift here is consistent with the elongation of the HO bond due to complexation. At the CCSD(T)/6-311++G(2df,2p) level, we report an HO bond distance of 1.004 Å for Br$^-$·HOCl, but only 0.964 Å for the HO bond in HOCl. The longer HO bond vibrates at a lower frequency. The HOCl bending mode (ν_2) is blue shifted by 186 cm^{-1}. This blue shift is in response to the opening of the HOCl angle by bromine complexation. The HOCl angle is opened by 1.1°, which allows the HOCl bend to occur at higher frequency. For the Br$^-$·ClOH conformation, we see similar effects in the calculated frequency results.

The calculated total energies for the Br$^-$·HOCl and Br$^-$·ClOH complexes are listed in Table 6. Also, the binding energies, which contain a zero-point correction, are included in Table 7. We see that the results have converged to give our best estimation of the energetics of these complexes at the CCSD-

TABLE 7: Relative Energies[a] for $Cl^-\cdot HOBr$, $Cl^-\cdot BrOH$, $Br^-\cdot HOCl$, $Br^-\cdot ClOH$, $Br^-\cdot HOBr$, and $Br^-\cdot BrOH$ Anion Clusters

	$Cl^-\cdot HOBr$		$Cl^-\cdot BrOH$	$Br^-\cdot HOCl$		$Br^-\cdot ClOH$	$Br^-\cdot HOBr$		$Br^-\cdot BrOH$
level of theory	$Cl^-\cdot BrOH$	$Cl^- + HOBr$	$Cl^- + HOBr$	$Br^-\cdot ClOH$	$Br^- + HOCl$	$Br^- + HOCl$	$Br^-\cdot BrOH$	$Br^- + HOBr$	$Br^- + HOBr$
MP2/6-31G(d)	2.5	25.8	23.3	11.0	25.4	14.4	−0.2	25.8	26.0
MP2/6-311G(d,p)	4.8	22.2	17.4	10.5	21.4	10.9	2.5	20.6	18.1
MP2/6-311++G(2df,2p)	2.0	25.4	23.4	8.5	21.7	13.3	0.9	21.6	20.7
CCSD(T)/6-31G(d)	3.1	25.1	22.0	11.5	24.5	13.0	0.9	24.6	23.7
CCSD(T)/6-311G(d,p)	5.3	21.7	16.4	11.1	20.7	9.6	3.3	19.8	16.5
CCSD(T)/6-311++G(2df,2p)	3.3	24.3	21.0	10.1	20.5	10.4	2.5	20.3	17.8
ΔZPE	−0.7	−1.0	−0.3	−0.7	−1.0	−0.3	−0.7	−0.8	−0.1
CCSD(T)/6-311++G(2df,2p) + ΔZPE	2.6	23.3	20.7	9.4	19.5	10.1	1.8	19.5	17.7

[a] Relative energies are reported in kcal mol^{-1}.

TABLE 8: Total Energies and Acidity of H·X (X = Cl, Br, OH, ClO, BrO)

	MP2			CCSD(T)			
species	6-31G(d)	6-311G(d,p)	6-311++G(2df,2p)	6-31G(d)	6-311G(d,p)	6-311++G(2df,2p)	exp
			Experimental Total Energies (Hartree)				
Cl^-	−459.66182	−459.74884	−459.82115	−459.66654	−459.71447	−459.78220	
Br^-	−2570.07908	−2572.95404	−2573.02273	−2570.06349	−2572.57231	−2572.62575	
HCl	−460.20215	−460.29297	−460.35776	−460.21159	−460.26332	−460.32251	
HBr	−2570.60758	−2573.48429	−2573.54019	−2570.59760	−2573.10791	−2573.14673	
OH^-	−75.51544	−75.59231	−75.70340	−75.52183	−75.58284	−75.68952	
ClO^-	−534.56623	−534.69131	−534.84610	−534.58066	−534.65186	−534.79552	
BrO^-	−2644.99033	−2647.90248	−2648.04766	−2644.98346	−2647.51481	−2647.63831	
H_2O	−76.19924	−76.28290	−76.33617	−76.20785	−76.27619	−76.32827	
HOCl	−535.16944	−535.30317	−535.42487	−535.18356	−535.26337	−535.37775	
HOBr	−2645.58910	−2648.51368	−2648.62514	−2645.58212	−2648.12635	−2648.21882	
			Acidity[a] (kcal mol^{-1})				
$HCl \rightarrow H^+ + Cl^-$	334.8	337.1	332.4	337.7	340.1	334.7	328.1
$HBr \rightarrow H^+ + Br^-$	327.8	328.9	320.9	331.3	336.1	323.1	318.3
$HOH \rightarrow H^+ + OH^-$	420.7	425.0	388.7	422.1	383.4	392.4	384.1
$HOCl \rightarrow H^+ + ClO^-$	371.1	376.5	355.8	370.9	376.3	358.0	349.2
$HOBr \rightarrow H^+ + BrO^-$	368.4	376.2	355.0	368.4	376.4	357.0	347.1

[a] Corrected for CCSD(T)/6-311G(d,p) zero-point energy.

(T)/6-311++G(2df,2p) level of computation. At this level, we find $Br^-\cdot HOCl$ to be the lowest energy conformation. From these results, we see that $Br^-\cdot HOCl$ is bound by 19.5 kcal mol^{-1}, whereas the $Br^-\cdot ClOH$ conformation is bound by 10.1 kcal mol^{-1}. We see that the $Br^-\cdot HOCl$ conformation is lower in energy by 9.4 kcal mol^{-1} relative to $Br^-\cdot ClOH$. Again, based upon the mechanism proposed by Chu and Chu,[11] the intermediate would most likely exist in the form $Br^-\cdot HOCl$.

It is interesting to compare the $Cl^-\cdot BrOH$ with $Br^-\cdot ClOH$. These anions are isoelectronic with the triatomic halide anions: $Cl^-\cdot BrF$ and $Br^-\cdot ClF$. In heteronuclear trihalide anions, the heaviest halide tends to occupy the central anion position.[30] A recent study of heteronuclear trihalide anions involving chlorine, bromine, and iodine has confirmed that isomers in which the heaviest atom occupies the central position are more stable than those in which the lighter atom occupies the central position.[31] In the case of $Cl^-\cdot BrOH$ and $Br^-\cdot ClOH$, the $Cl^-\cdot BrOH$ is more stable by 9.3 kcal mol^{-1} at the CCSD(T)/6-311++G(2df,2p) level of theory. This is consistent with energy differences for $Cl^-\cdot BrCl$ and $Br^-\cdot ClCl$ of 10.6 kcal mol^{-1} and $Br^-\cdot BrCl$ and $Br^-\cdot ClBr$ of 9.4 kcal mol^{-1} at the MP3/MID-4*//MP2/MIDI-4*+ level of theory.[31]

D. $Br^-\cdot HOBr$ vs $Br^-\cdot BrOH$. The species of interest in this study is the complex formed between bromine anions and hypobromous acid. Again, we have considered two possible conformers, the first with the bromine anion complexing through the hydrogen of HOBr and the second with the bromine anion complexing through the bromine atom of HOBr. We report fully optimized geometries at all levels of calculation in Table 4 for this system and, accordingly, our best estimate as to the equilibrium geometry of these complexes occurs at the CCSD(T)/6-311++G(2df,2p) level of calculation. When comparing the geometries of these complexes, we also include the $Br^-\cdot H_2O$ geometry optimizations as another point of comparison. In the case of $Br^-\cdot HOBr$, we see a shortening of the Br−H bond relative to $Br^-\cdot H_2O$. Our CCSD(T)/6-311++G(2df,2p) result estimates this bond to be about 0.2 Å shorter in $Br^-\cdot HOBr$ than in $Br^-\cdot H_2O$. This indicates that the bromine anion is more strongly bound to HOBr than to H_2O. Also, we note a lengthening of the HO bond due to bromine complexation. In $Br^-\cdot H_2O$, the H′O bond length is 0.979 Å, whereas in $Br^-\cdot HOBr$, the H′O bond length is predicted to be 1.00 Å at the CCSD(T)/6-311++G(2df,2p) level. Another interesting effect of the bromine complexation is the opening of the HOBr angle relative to uncomplexed HOBr. At the CCSD(T)/6-311++G(2df,2p) level, we calculate the HOBr angle in HOBr to be 102.9°, whereas this angle opens up to 103.6° in $Br^-\cdot HOBr$. This 0.7° opening is due to the additional repulsion added by the complexation of the bromine atom.

For the $Br^-\cdot BrOH$ case, we also note some more subtle effects of the bromine complexation through the bromine of HOBr. First, we see that the Br−Br bond is predicted to be 2.706 Å at the CCSD(T)/6-311++G(2df,2p) level. Complexation through the hydrogen of HOBr also opened the HOBr bond angle relative to complexation through the bromine. At the CCSD(T)/6-311++G(2df,2p) level, we see the HOBr bond angle open from 100.0° in $Br^-\cdot BrOH$ to 103.6° in $Br^-\cdot HOBr$.

Our frequency calculations in Table 5 are reported at the CCSD(T)/6-311G(d,p) level of theory. At this level, we report the HO stretch in $Br^-\cdot HOBr$ to be red shifted by 633 cm^{-1}. This can be explained by the lengthening of the OH bond in $Br^-\cdot HOBr$ relative to uncomplexed HOBr. The OH bond is 0.04 Å longer; thus, the bond stretches at the red shifted frequency.

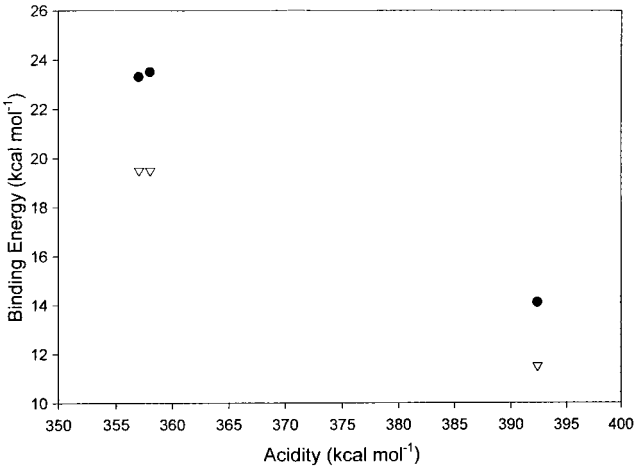

Figure 1. Plot of $X^-\cdot HOY$ (where X = Cl or Br and Y = H, Cl, Br) binding energy versus acidity of the HOY monomer. Closed circle represents $Cl^-\cdot HOY$ and open triangle represents $Br^-\cdot HOY$.

Tables 6 and 7 contain the results of the energetic studies for these conformers. At the CCSD(T)/6-311++G(2df,2p) level of theory, the trends in the relative energetics of these complexes show that the lowest energy structure of the two conformers places the halogen in complexation through the hydrogen of the acid. We also find that $Br^-\cdot BrOH$ is stable to dissociation into Br^- and HOBr by 17.7 kcal mol^{-1}. As well, we note that $Br^-\cdot HOBr$ is stable to the same dissociation pathway by 19.5 kcal mol^{-1}. There is a 1.8 kcal mol^{-1} difference in energy between $Br^-\cdot BrOH$ and $Br^-\cdot HOBr$. These results are quite interesting. In solution,[17,29] the reaction of HOBr with ionized HBr

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$$

is consistent with the involvement of a $Br^-\cdot BrOH$ intermediate which, upon attack of H^+, yields the products $Br_2 + H_2O$, viz.

$$Br^-\cdot BrOH + H^+ \rightarrow Br_2 + H_2O$$

It could be the case that the energy of solvation may drive the Br^- + HOBr reaction toward the $Br^-\cdot BrOH$ instead of the $Br^-\cdot HOBr$ intermediate.

To better understand the strength of the $X^-\cdot HOY$ (where X, Y = H, Cl, or Br) bond, we have calculated the acidities for HOY. The calculated acidities are reported in Table 8. A comparison of the calculated acidities with experimental known values show that the rms error between the values is 8.8 kcal mol[1] at the CCSD(T)/6-311++G(2df,2p) level of theory. Nevertheless, the calculated acidities follow the same trend as the experimental reported values. As shown in Figure 1, there is a trend in the binding energies of the complex with the acidity for both chlorine and bromine anions. The data suggest that the more acidic the hydrogen, the more likely that the halogen anion will be tightly bound to the HOX. The data also indicate that the binding energies for $X^-\cdot HOCl$ and $X^-\cdot HOBr$, where X = Cl and Br, are very close in energy because the acidities of HOCl and HOBr are close in value. Indeed, the calculations from Table 7 suggest that these binding energies are close in energy.

IV. Conclusions

Ab initio molecular orbital calculations have been employed to probe the molecular geometries, vibrational frequencies, and energetics of $Cl^-\cdot HOBr$, $Cl^-\cdot BrOH$, $Br^-\cdot HOCl$, $Br^-\cdot ClOH$, $Br^-\cdot HOBr$, and $Br^-\cdot HOBr$ anionic complexes. For the $Cl^-\cdot HOBr$ complexes, we predict that Cl^- would most likely be bound to the hydrogen of HOBr. The binding energy of this structure is predicted to be 23.2 kcal mol^{-1}. For the $Br^-\cdot HOCl$ type complexes, we find that the Br^- most likely complexes through the hydrogen, as well. This complex is bound by 19.5 kcal mol^{-1}. The results of both sets of complexes are in qualitative agreement with similar results from studies on $Cl^-\cdot HOCl$ complexes.[15] For $Br^-\cdot HOBr$ type complexes, we find that the minimum energy structure involves complexation through the hydrogen of the acid. The $Br^-\cdot HOBr$ complex is predicted to be bound by 19.5 kcal mol^{-1}.

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References and Notes

(1) Anderson, J. G. *Annu. Rev. Phys. Chem.* **1987**, *38*, 489.
(2) Hamill, P.; Toon, O. B. *Phys. Today* **1991**, *44*, 34.
(3) Rowland, F. S. *Annu. Rev. Phys. Chem.* **1991**, *42*, 731.
(4) Randeniya, L. K.; Vohralik, P. F.; Plumb, K.; Ryan, K. R. *J. Geophys. Res. Atmos.* **1997**, *102*, 23543.
(5) Hanson, D. R.; Ravishankara, A. R. *Geophys. Res. Lett.* **1995**, *22*, 385.
(6) Hanson, D. R.; Ravishankara *J. Phys. Chem.* **1992**, *96*, 2682.
(7) Abbatt, J. P. D.; Molina, M. *Geophys. Res. Lett.* **1992**, *19*, 461.
(8) Opplinger, R.; Allanic, A.; Rossi, M. J. *J. Phys. Chem. A* **1997**, *101*, 1903.
(9) Abbatt, J. P. D. *Geophys. Res. Lett.* **1994**, *21*, 665.
(10) Allanic, A.; Opplinger, R.; Rossi, M. J. *J. Geophys. Res.* **1997**, *102*, 23529.
(11) Chu, L.; Chu, L. *J. Phys. Chem. A* **1999**, *103*, 691.
(12) Abbatt, J. P.; Bayer, K. D.; Fucaloro, A. F.; McMahon, J. R.; Wooldridge, P. J.; Zhang, R.; Molina, M. J. *J. Geophys. Res.* **1992**, *97*, 15819.
(13) Abbatt, J. P. D.; Molina, M. *J. Phys. Chem.* **1992**, *96*, 7074.
(14) Haas, B. M.; Crellin, K. C.; Kuwata, K. T.; Okumura, M. *J. Phys. Chem.* **1994**, *98*, 6740.
(15) Francisco, J. S. *Chem. Phys. Lett.* **1996**, *260*, 485.
(16) Richardson, S. L.; Francisco, J. S.; Mebel, A. M.; Morokuma, K. *Chem. Phys. Lett.* **1997**, *270*, 395.
(17) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.
(18) Choi, J.; Kuwata, K.; Cao, Y.; Okumura, M. *J. Phys. Chem. A* **1998**, *102*, 503.
(19) Cambariza, J. E.; Kestner, N. R.; Jortner, J. *J. Phys. Chem.* **1994**, *100*, 2851.
(20) Xantheas, S. *J. Phys. Chem.* **1996**, *100*, 9703.
(21) Ayotte, P.; Weddle, G. H.; Kim, J.; Johnson, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 12361.
(22) Zhao, X. G.; Gonzalez-Lafont, A.; Truhlar, D. G.; Steckler, R. *J. Chem. Phys.* **1991**, *94*, 5544.
(23) Schindler, T.; Berg, C.; Borg, C.; Niedner-Schatteburg, G.; Bondybex, V. E. *J. Phys. Chem.* **1990**, *99*, 12434.
(24) Hirota, K.; Mizuse, S.; Yanabe, S. *J. Phys. Chem.* **1988**, *92*, 3943.
(25) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 517.
(26) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; National Bureau of Standards: Gaithersburg, MD, 1972; Vol. 1, pp 1−160.
(27) Ayotte, P.; Bailey, C. G.; Weddle, G. H.; Johnston, M. A. *J. Phys. Chem. A* **1998**, *102*, 3067.
(28) Schwager, I.; Arkell, A. *J. Am. Chem. Soc.* **1967**, *89*, 6006.
(29) Wang, T. X.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 1050.
(30) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 577.
(31) Ogawa, Y.; Takahashi, O.; Kikuchi, O. *J. Mol. Struct. (THEOCHEM)* **1998**, *429*, 187.