

# The Gas-Phase Hydrogen Bond Complexes between Formic Acid with Hydroxyl Radical: A Theoretical Study

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*We report a theoretical study on seven radical hydrogen bond complexes between syn-HCOOH and OH and eight radical hydrogen bond complexes between anti-HCOOH and OH, that have been carried out by using the B3LYP, MP2, QCISD, and CCSD(T) theoretical approaches with the 6-311 + G(2df,2p) basis set. In all cases, the bonding features were analysed using the atoms in molecules (AIM) theory by Bader and the natural bond orbital (NBO) partition scheme by Weinhold et al. We have found twelve complexes having a single hydrogen bond and three complexes presenting a cyclic structure with multiple bonds, pointing out the*

*existence of a cooperative effect. One of them presents a bound O...O interaction producing a stabilisation effect. The stability of these complexes has been calculated to be in the  $-0.81$  and  $-5.96$  kcal mol<sup>-1</sup> range and their possible implication in the HCOOH plus OH reaction is also discussed.*

*Finally, we also report the computed harmonic vibrational frequencies of the two O-H stretching modes and the HOC out-of-plane wagging mode, along with the frequency red-shifts originated by the complex formation and the corresponding computed intensity ratio relative to the monomers.*

## Introduction

Despite the fact that hydrogen bond complexes have been known for many years, they still attract a lot of interest due to their importance in several areas of chemistry. A great amount of research work is still devoted to this issue, focussing their attention in complexes formed between two neutral molecules and complexes formed between a neutral molecule and an ion. Several books exist in the literature dealing with hydrogen bonds from different points of view,<sup>[1–3]</sup> and very recently different aspects of these compounds have been reviewed.<sup>[4–7]</sup> However, very less attention has been devoted to the radical–molecule hydrogen bond complexes and only recently there have been reported in the literature studies on the O<sub>x</sub>H radical complexes with different species.<sup>[8–16]</sup> These compounds play an important role in the chemistry of Earth atmosphere. It has been recently pointed out that the formation of intermediate or pre-reactive radical hydrogen bond complexes may influence considerably the kinetics of the reaction, and that the forces due to hydrogen bonds are sufficient to influence the collision dynamics as the reagents approach to each other.<sup>[17–20]</sup>

Following the theory of atoms in molecules by Bader,<sup>[21]</sup> Popelier<sup>[22, 23]</sup> defined an hydrogen bond according the topological properties of the electron density. From a more phenomenological point of view, Steiner<sup>[4]</sup> considers an X–H...Y interaction as hydrogen bond if a) it constitutes a local bond and b) X–H acts as a proton donor to Y. Here, X acts as a donor and Y as acceptor and the hydrogen bond complex can, at least in principle, be understood as an incipient proton transfer reaction from X–H to Y. There is a formal or real electron transfer whose direction is reverse to the direction of proton donation.

Fonseca et al.<sup>[24–26]</sup> pointed out that this charge transfer is provided by the interaction of the lone pair of the acceptor atom with the unoccupied  $\sigma^*$  orbital of the X–H donor.

The view that the hydrogen bond can be understood as an incipient proton transfer reaction from X–H to Y may shed some light in the study and the comprehension of chemical reactivity involving hydrogen or proton transfer and naturally, the consideration of the corresponding pre-reactive hydrogen bond complexes is of interest.

As a part of our research on the gas-phase reactions among HO<sub>x</sub> radicals with different species having interest in atmospheric chemistry, we present in this paper a theoretical study on the gas phase hydrogen bond complexes between formic acid and the OH radical. Formic acid is the most abundant carboxylic acid in the troposphere<sup>[27]</sup> and their main sink is the reaction with hydroxyl radical. In this work we will analyse the structure and stability of these complexes, which are the first stage of the reaction.<sup>[28]</sup>

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## Computational Details

All calculations carried out in this work have been done using the 6-311 + G(2df,2p) basis set.<sup>[29]</sup> In a first step, the geometry optimizations for all stationary points were performed using the hybrid density functional B3LYP method.<sup>[30]</sup> The harmonic vibrational frequencies were also calculated at the same level of theory in order to verify the nature of the corresponding stationary point (minima or transition state), and to provide the zero-point vibrational energy (ZPE) and the thermodynamic contributions to the enthalpy for  $T = 298$  K. In a second step, we have reoptimized all stationary points at the QCISD<sup>[31]</sup> level of theory. In addition, and for two stationary points of interest, we have also performed additional geometry optimizations and vibrational analysis at the MP2<sup>[32–34]</sup> level. Final energies were obtained by performing single point CCSD(T) calculations<sup>[35–38]</sup> at the geometries obtained at both B3LYP and QCISD levels of theory. In addition, at the B3LYP optimized geometries, the basis set superposition error (BSSE) have been computed, at the CCSD(T) level of theory, for each compound according to the procedure reported by Boys and Bernardi,<sup>[39]</sup> properly taking into account the fragment relaxation.<sup>[40]</sup> These calculations were done using the Gaussian 98 program package,<sup>[41]</sup> and the absolute energies along with the Cartesian coordinates of each stationary point are given as supporting information.

At the B3LYP6-311 + G(2df,2p) level of theory, we have analyzed the bonding features of the complexes by using the atoms in molecules (AIM) theory by Bader.<sup>[21]</sup> The AIMPACK package<sup>[42]</sup> was used to obtain the topological properties of the wave function. The charge distribution were obtained following the natural bond orbital (NBO) partitioning scheme by Weinhold and co-workers.<sup>[43]</sup>

## Results and Discussion

From an electronic point of view, the OH radical can approach formic acid in two different ways as displayed in Figure 1. In the first one, (see Figure 1 a), the electronic density of the unpaired electron of the OH radical is in the same plane containing the HCCOH molecule and therefore we name this as  $\sigma$  or symmetric approach. In the second one, the unpaired electron of the OH radical lies in a plane perpendicular to the plane containing the HCOOH moiety, and we label this as  $\pi$  or asymmetric approach (see Figure 1 b). This situation leads to two different electronic features of the formed complexes. Thus, when the resulting complex is planar, the symmetric approach will lead to duplet

electronic states of  $A'$  symmetry, while the asymmetric approach will lead to duplet electronic states of  $A''$  symmetry.

Moreover, if we take into account that hydroxyl radical can approach formic acid in different directions; we will find several kinds of radical complexes. According to the electronic character of the groups involved in the electronic interactions, we can face situations in which the proton donor X is the oxygen of the hydroxyl group or the carbon of the acid or the OH radical, while the acceptor atom may be the two oxygen atoms of the formic acid or the oxygen of the hydroxyl radical. The different donor or acceptor abilities of these groups result in different stabilities of the formed complexes with different electronic and spectroscopic features. In addition, we can also find situations in which combined interactions occur, enhancing thus the stability of the corresponding compound.

## Geometric and Energetic Considerations

We have found nine stationary points formed between syn-HCOOH and OH radical and eight hydrogen bond complexes formed between anti-HCOOH and OH radical. The corresponding structures along with the most relevant geometrical parameters are displayed in Figures 2 and 4, which show that the optimized values obtained at the different levels of theory agree very well. The B3LYP and CCSD(T) complex stabilities computed at the B3LYP optimized geometry are collected in Tables 1 and 3, which show that the values obtained at both levels of treatment agree qualitatively. These values agree also very well with those obtained at the CCSD(T) computed at the QCISD optimized geometries (see Table S3 of supplementary material). Therefore, and for the sake of clarity, these later ones are included only as supplementary material and the main discussions will refer to the calculations carried out on the B3LYP6-311 + G(2df,2p) optimized geometries.

Tables 1 and 3 show that, depending on the theoretical method, the stability of a given complex differs among 0.3 and 2.6 kcal mol<sup>-1</sup> and in what follows we will only consider the CCSD(T) values taking into account the BSSE corrections.

Figure 3 shows density difference maps for some selected complexes, which are obtained by subtracting to the total electronic density, the electronic density of each fragment (HCOOH and OH, respectively). The topological parameters are contained in Tables 2 and 4, which display the distances of the

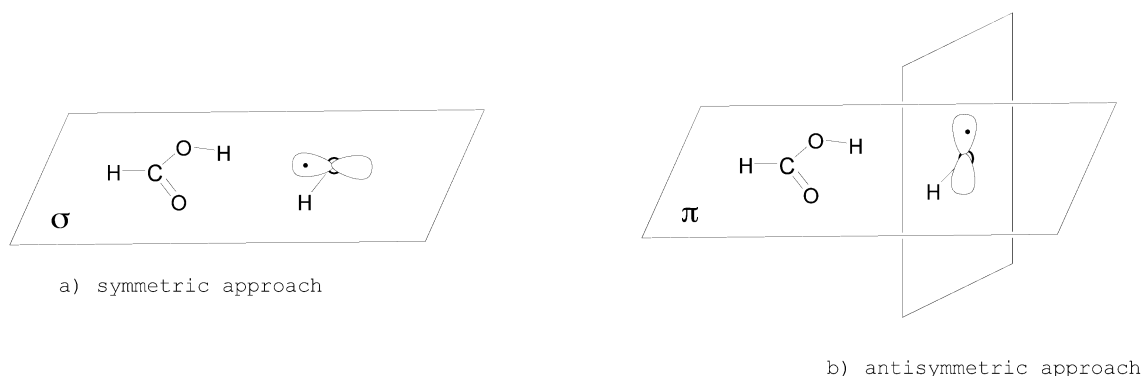
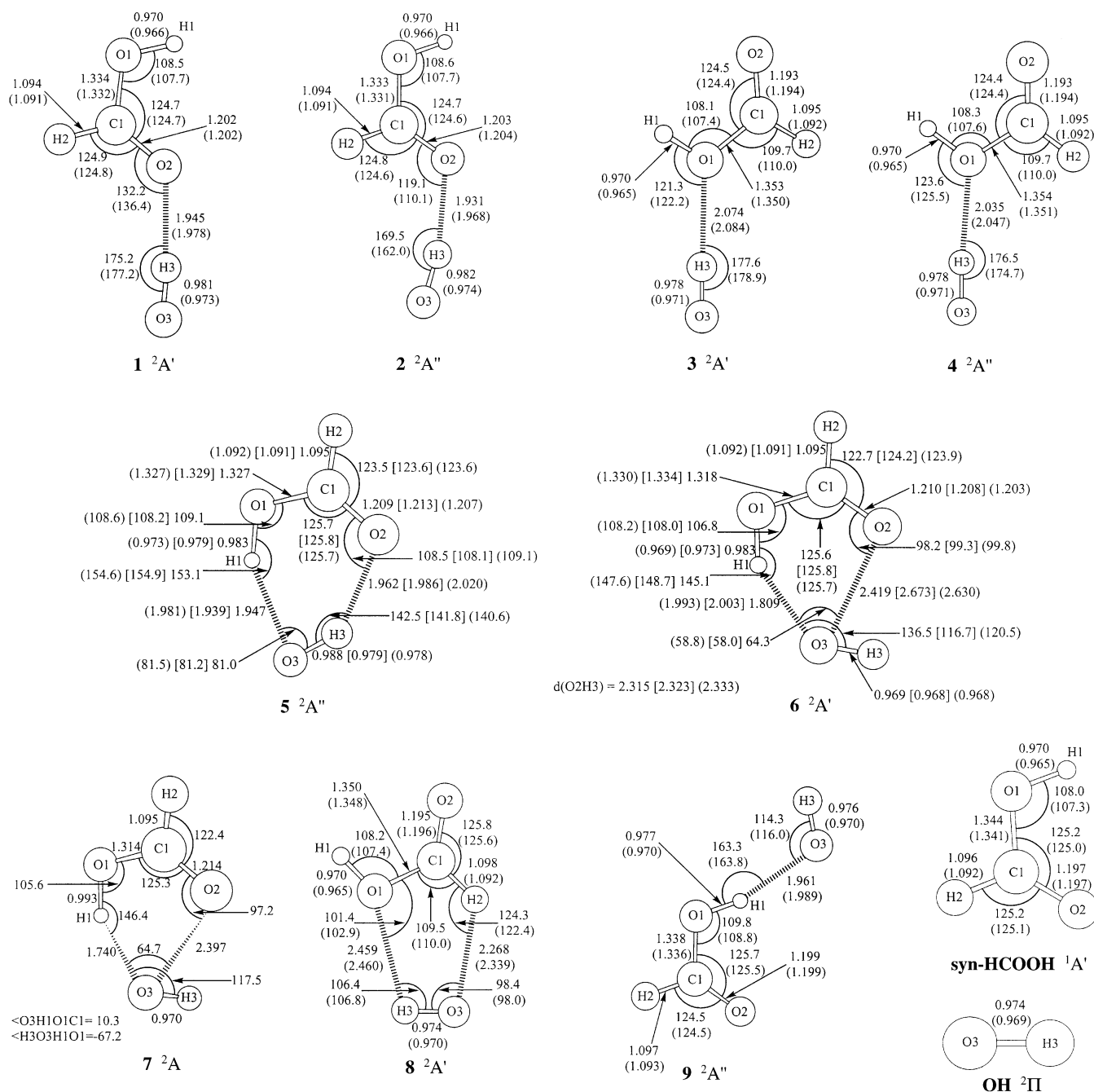


Figure 1. Schematic ways of OH radical approaching formic acid.



**Figure 2.** Selected geometrical parameters of the B3LYP6-311 + G(2df,2p) optimized geometries for complexes formed between syn-HCOOH and OH. The MP2/6-311 + G(2df,2p) and QCISD/6-311 + G(2df,2p) optimized geometrical parameters are given in brackets and parentheses, respectively. Distances are given in Ångstroms and angles in degrees.

atoms involved in the complex interaction to the bond critical points (bcp), the electron density ( $\rho$ ), and the Laplacian of the electron density ( $\nabla^2\rho$ ) at the bcp. These tables also contain the overall NBO charge transfer (CT, expressed in millielectrons, me) between the HCOOH and OH units, which are involved in the complex formation. This is computed summing up the NBO atomic charges on either of the individual monomer. Because of the sum of these charges in the isolated compounds must be zero, these CT values provide an estimation of the charge transferred between HCOOH and OH in the complex formation.

## Complexes Formed between syn-HCOOH and OH

Figure 2 shows the O—H...O bond distances range among 1.740 and 2.459 Å, which suggests different features of the hydrogen bond interaction. In complexes 1, 2, 3, and 4 the hydroxyl radical acts as a donor and they involve a single hydrogen bond as indicated in the topological properties displayed in Table 2. In fact, complexes 1( $^2A'$ ) and 2( $^2A''$ ) are planar and correspond to the same structure, where the acceptor is the oxygen of the

**Table 1.** Calculated zero-point vibrational energies (ZPVE in kcal mol<sup>-1</sup>), absolute entropies (*S* in eu) and the stabilities ( $\Delta E$  and  $\Delta H$  in kcal mol<sup>-1</sup>) for various complexes between syn-HCOOH and OH radical.

Structure	ZPVE <sup>[a]</sup>	<i>S</i> <sup>[a]</sup>	B3LYP		CCSD(T)	
			$\Delta E^{[a,c]}$	$\Delta H^{[a,c]}$	$\Delta E^{[b,c]}$	$\Delta H^{[b,c]}$
syn-HCOOH + OH	26.4	101.9	0.00	0.00	0.00	0.00
1	<sup>2</sup> A' 28.0	80.1	-4.98	-3.68	-5.28	-3.98
			(-4.14)	(-2.84)	(-4.44)	(-3.14)
2	<sup>2</sup> A'' 28.1	79.5	-5.18	-3.85	-5.52	-4.20
			(-4.31)	(-2.98)	(-4.65)	(-3.33)
3	<sup>2</sup> A' 27.7	81.8	-2.54	-1.42	-3.16	-2.04
			(-1.78)	(-0.66)	(-2.4)	(-1.28)
4	<sup>2</sup> A'' 27.7	81.3	-2.90	-1.76	-3.54	-2.40
			(-2.10)	(-0.96)	(-2.74)	(-1.60)
5	<sup>2</sup> A'' 28.3	74.0	-7.95	-6.73	-8.53	-7.31
			(-6.6)	(-5.38)	(-7.18)	(-5.96)
6 <sup>[d]</sup>	<sup>2</sup> A' 28.0	72.1	-7.75	-7.09	-5.60	-4.93
			(-6.33)	(-5.67)	(-4.18)	(-3.51)
7	<sup>2</sup> A 28.4	73.0	-8.57	-7.28	-6.01	-4.72
			(-6.83)	(-5.54)	(-4.27)	(-2.98)
8	<sup>2</sup> A' 27.2	83.5	-2.03	-1.12	-2.44	-1.53
			(-1.31)	(-0.4)	(-1.72)	(-0.81)
9 <sup>[d]</sup>	<sup>2</sup> A'' 27.4	77.1	-3.94	-3.53	-4.47	-4.05
			(-3.16)	(-2.75)	(-3.69)	(-3.27)

[a] Values computed at the B3LYP6-311 + G(2df,2p) level of theory. [b] Single point CCSD(T)/6-311 + G(2df,2p) energies calculated at the B3LYP6-311 + G(2df,2p) optimized geometries. [c] The values in parentheses include BSSE corrections computed at CCSD(T)/6-311 + G(2df,2p) level of theory. [d] Correspond to a transition state.

carbonyl group. Both differentiate in the orientation of the unpaired electron. It is mainly located on the oxygen of the hydroxyl group, which is far apart from the hydrogen bond interaction, having a minor influence on the stability of both complexes. Therefore, the computed C=O...H bond lengths (1.945 and 1.931 Å, Figure 2) and their stability ( $\Delta H = -3.14$  and  $-3.33$  kcal mol<sup>-1</sup>, best values in Table 1) are very close. Consequently, the topological values are very similar ( $\rho = 0.0232$  and  $0.0251$  a.u. and  $\nabla^2\rho = 0.0825$  and  $0.0845$  a.u. for **1** (<sup>2</sup>A') and **2**, (<sup>2</sup>A'')) respectively).

Complexes **3**(<sup>2</sup>A') and **4**(<sup>2</sup>A'') present the same features as complexes **1** and **2**, but in this case the acceptor group is the hydroxyl belonging to the formic acid moiety. Their O...H bond lengths are larger (2.074 and 2.035 Å, respectively) and they are less stable ( $\Delta H = -1.28$  and  $-1.60$  kcal mol<sup>-1</sup>, respectively, the best values in Table 1), pointing out that the hydroxyl group is a worse acceptor. Accordingly the values of the density and its laplacian at the corresponding bcp are smaller (see Table 2).

The remaining complexes (**5**, **6**, **7**, and **8**) possess cyclic structure (see Figure 2), which suggests the existence of multiple interactions. In complex **5** the relative orientation of the hydroxyl radical with respect to the formic acid moiety allows a multiple interaction in which two donor-acceptor pairs can be envisaged, namely the O-H...O=C(OH)H and the H(O)C-O-H...O-H pairs, forming two hydrogen bonds with distances 1.962 and 1.947 Å, respectively. This leads to a six-membered ring structure and makes both moieties (HCOOH and OH) to act as a donor and acceptor simultaneously. The complex is planar and the unpaired electron resides in an orbital perpendicular to the molecular plane. Therefore it must be classified as a <sup>2</sup>A'' ( $\pi$  symmetry). The

**Table 2.** Calculated topological properties of the bond critical points of interest<sup>[a]</sup> and NBO net atomic charge transfer<sup>[b]</sup> for the complexes between syn-HCOOH and OH.

Complex X-Y Bond/Ring		$r_X$ [Å] <sup>[c]</sup>	$r_Y$ [Å] <sup>[d]</sup>	$\rho_b$ [a.u.] <sup>[e]</sup>	$\nabla^2\rho_b$ [a.u.] <sup>[f]</sup>	$q_{\text{HCOOH}}$ [me] <sup>[g]</sup>
1	H3O2	0.695	1.252	0.0232	0.0825	13.1
2	H3O2	0.685	1.248	0.0251	0.0845	16.0
3	H3O1	0.759	1.315	0.0172	0.0623	6.8
4	H3O1	0.740	1.294	0.0189	0.0683	7.5
5	H1O3	0.685	1.263	0.0269	0.0816	-11.7
	H3O2	0.711	1.257	0.0262	0.0840	
	(3,1)			0.0134	0.0533	
6	H1O3	0.650	1.162	0.0312	0.1152	108.4
	O2O3	1.170	1.248	0.0255	0.1063	
	(3,1)			0.0173	0.0723	
7	H1O3	0.594	1.147	0.0409	0.1222	101.2
	O2O3	1.236	1.162	0.0270	0.1113	
	(3,1)			0.0192	0.0820	
8	H2O3	0.962	1.309	0.0125	0.0471	24.7
	H3O1	1.046	1.433	0.0095	0.0361	
	(3,1)			0.0080	0.0372	
9	H1O3	0.691	1.272	0.0236	0.0771	8.45

[a] Determined from Bader topological analysis of the B3LYP6-311 + G(2df,2p) wave function. Atom numbering refers to Figure 2 and (3,1) stands for a bond critical point of ring-type. [b] Determined from NBO population analysis of the B3LYP6-311 + G(2df,2p) wave function. [c] The distance between the bond critical point and the X atom. [d] The distance between the bond critical point and the Y atom. [e] Electronic charge density at the bond critical point. [f] Laplacian of  $\rho_b$ . [g] Net charge (in millielectrons) over the HCOOH moiety.

**Table 3.** Calculated zero-point vibrational energies (ZPVE in kcal mol<sup>-1</sup>), absolute entropies (*S* in eu) and the stabilities ( $\Delta E$  and  $\Delta H$  in kcal mol<sup>-1</sup>) for various complexes between anti-HCOOH and OH.

Structure	ZPVE <sup>[a]</sup>	<i>S</i> <sup>[a]</sup>	B3LYP		CCSD(T)	
			$\Delta E^{[a,c]}$	$\Delta H^{[a,c]}$	$\Delta E^{[b,c]}$	$\Delta H^{[b,c]}$
anti-HCOOH + OH	26.2	102.1	0.00	0.00	0.00	0.00
10	<sup>2</sup> A' 27.9	79.9	-5.14	-3.81	-5.42	-4.09
			(-4.33)	(-3.00)	(-4.61)	(-3.28)
11	<sup>2</sup> A'' 28.0	78.7	-5.44	-4.07	-5.86	-4.49
			(-4.56)	(-3.19)	(-4.98)	(-3.61)
12	<sup>2</sup> A' 27.9	79.8	-5.26	-3.94	-5.62	-4.30
			(-4.44)	(-3.12)	(-4.80)	(-3.48)
13	<sup>2</sup> A'' 27.9	79.6	-5.14	-3.82	-5.51	-4.19
			(-4.33)	(-3.01)	(-4.70)	(-3.38)
14	<sup>2</sup> A' 27.4	82.8	-3.19	-2.11	-3.85	-2.78
			(-2.53)	(-1.45)	(-3.19)	(-2.12)
15	<sup>2</sup> A'' 27.5	81.7	-3.31	-2.19	-3.96	-2.85
			(-2.57)	(-1.45)	(-3.22)	(-2.11)
16	<sup>2</sup> A'' 27.2	84.8	-4.54	-3.47	-5.03	-3.96
			(-3.80)	(-2.73)	(-4.29)	(-3.19)
17	<sup>2</sup> A'' 27.4	80.7	-5.22	-4.12	-5.70	-4.60
			(-4.44)	(-3.34)	(-4.92)	(-3.82)

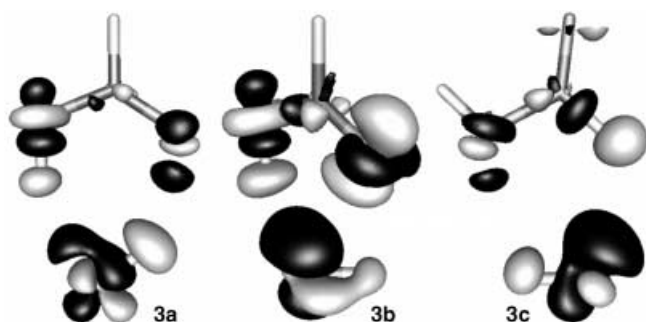
[a] Values computed at the B3LYP6-311 + G(2df,2p) level of theory. [b] Single point CCSD(T)/6-311 + G(2df,2p) energies calculated at the B3LYP6-311 + G(2df,2p) optimized geometries. [c] The values in parentheses include BSSE corrections computed at CCSD(T)/6-311 + G(2df,2p) level of theory.

geometric restriction imposed by the six-membered ring structure imply O-H...O angles far from linearity (142.5° and 153.1°, respectively). In addition, the hydrogen-bond directionality at the acceptor sides (C-O...H = 108.5° and H...OH = 81.0°) is far from being optimum.<sup>[4]</sup> The topological analysis, displayed

**Table 4.** Calculated topological properties of the bond critical points of interest<sup>[a]</sup> and NBO net atomic charge transfer<sup>[b]</sup> for the complexes between anti-HCOOH and OH.

Complex	X–Y Bond/Ring	$r_x$ [Å] <sup>[c]</sup>	$r_y$ [Å] <sup>[d]</sup>	$\rho_b$ [a.u.] <sup>[e]</sup>	$\nabla^2\rho_b$ [a.u.] <sup>[f]</sup>	$q_{\text{HCOOH}}$ [me] <sup>[g]</sup>
10	H3O2	0.694	1.251	0.0236	0.0831	14.0
11	H3O2	0.685	1.246	0.0259	0.0858	17.3
12	H3O2	0.702	1.261	0.0223	0.0786	13.8
13	H3O2	0.708	1.266	0.0217	0.0767	13.0
14	H3O1	0.796	1.343	0.0149	0.0543	5.8
15	H3O1	0.770	1.313	0.0170	0.0622	5.8
16	H1O3	0.692	1.266	0.0231	0.0785	– 18.0
17	H1O3	0.675	1.257	0.0254	0.0828	– 21.7

[a] Determined from Bader topological analysis of the B3LYP6-311 + G(2df,2p) wave function. Atom numbering refers to Figure 4. [b] Determined from NBO population analysis of the B3LYP6-311 + G(2df,2p) wave function. [c] The distance between the bond critical point and the X atom. [d] The distance between the bond critical point and the Y atom. [e] Electronic charge density at the bond critical point. [f] Laplacian of  $\rho_b$ . [g] Net charge (in millielectrons) over the HCOOH moiety.

**Figure 3.** Electron density difference map for the **5** (3a), **7** (3b) and **8** (3c) complexes. Grey regions represent depleted electron density and black regions correspond to increased electron density. The contours shown are 0.003 for **5** and **7** and 0.001 for **8**.

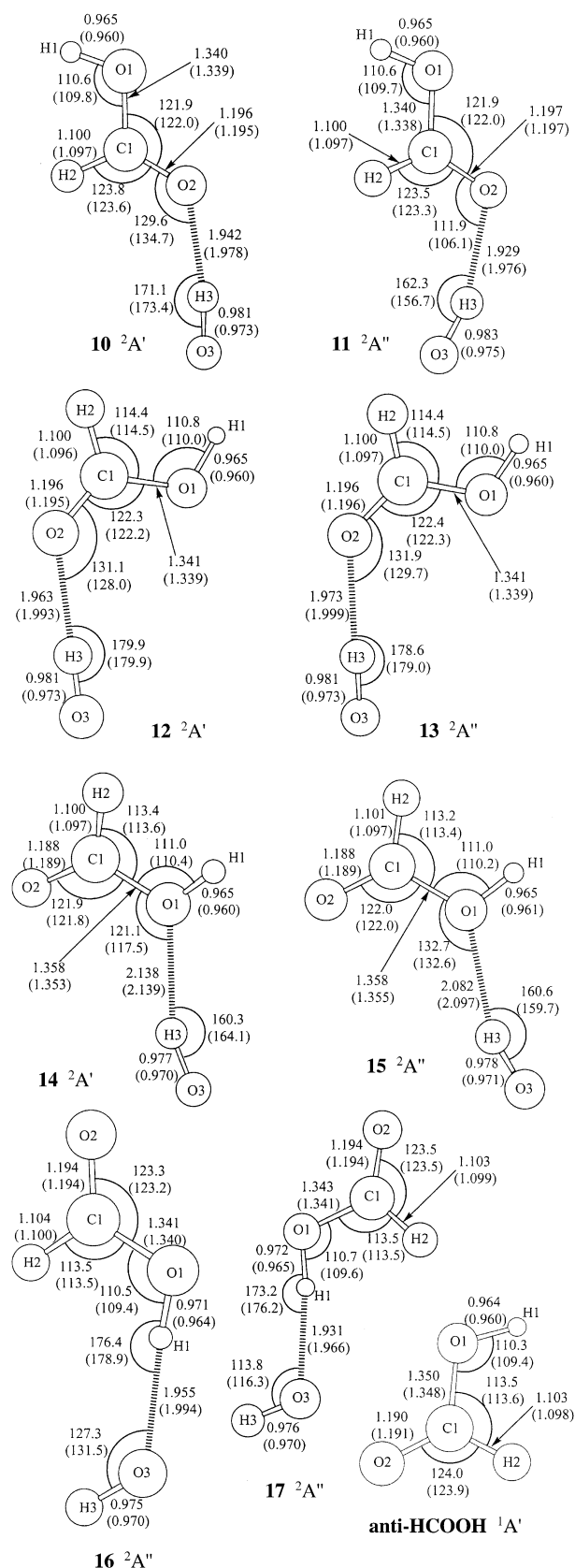
in Table 3, corroborates the existence of two hydrogen bonds but also points out the existence of a ring bcp,<sup>[21]</sup> which enhances the stability of the complex and points out the existence of a cooperative effect. Thus, despite this geometric restriction, this is the most stable hydrogen bond complex ( $\Delta H = -5.96 \text{ kcal mol}^{-1}$ , see Table 2). Here it is also interesting to draw attention to the geometrical changes produced on the HCOOH and OH moieties as a result of the hydrogen bond interactions. Comparing the geometrical parameters displayed in Figure 2, we observe a lengthening of the C=O distance by 0.012 Å, a shortening of the C–O distance by 0.017 Å, and a lengthening of both O–H bond distances by about 0.014 Å. This suggests a weak electron delocalization associated with a typical resonance assisted hydrogen bonding mechanism (RAHB),<sup>[44]</sup> which is consistent with the structure of complex **5** having a ring bcp.

In complex **6**, HCOOH and OH have the same relative orientation than in complex **5**, but the unpaired electron resides in an orbital located in the molecular plane ( $^2A'$  state or  $\sigma$  symmetry). From a structural point of view, Figure 2 shows that the H1...O3 bond length (1.809 Å) is shorter than the corresponding bond length in structure **5**, but the O2...H3 distance is

much larger (2.315 Å). Here, the results obtained at MP2 and QCISD levels of theory (see Figure 2) show a larger H1O3 and O2O3 bond lengths (by about 0.2 Å) and a smaller H1O3H3 angle. The topological analysis of the B3LYP wave function, displayed in Table 2, indicates that H1...O3 is a true hydrogen bond but there is not a hydrogen bridge between O2 and H3. Rather, we have found a bcp between O2 and O3, which makes complex **6** as a five-membered ring. A ring bcp was also found as indicated in Table 2. Very interesting here is the fact that at both, B3LYP and MP2 levels of theory, diagonalization of the Hessian matrix shows that structure **6** ( $^2A'$ ) has an imaginary frequency and therefore it is not a true minima but a transition state. Moreover, the analysis of the transition vector indicates a flip of the OH moiety out of the molecular plane. At this point it is also interesting to compare structures **5** and **6** (see Figure 2) with the hydrogen bond complex (RC-I) reported recently by Galano et al.<sup>[20]</sup> It looks like the authors obtained the  $^2A''$  electronic state at BH&HLYP and MP2 levels of theory, but the  $^2A'$  state at B3LYP, MP4 and QCISD level. However, there is any discussion about the symmetry of the corresponding electronic state.

Following the direction of the transition vector in complex **6**, we have found complex **7**, in which the OH radical is about 67° out of the HCOOH plane (see Figure 2). Complex **7** is also a five-membered ring, and, as in structure **6**, the topological analysis of the wave function (see Table 2) indicates the existence of only one hydrogen bond (H1...O3), a bcp between the oxygen of the carbonyl (O2) and the oxygen of the hydroxyl radical (O3) and a ring bcp. The topological properties of this O2...O3 bcp ( $\rho = 0.0270 \text{ a.u.}$  and  $\nabla^2\rho = 0.1113 \text{ a.u.}$ , see Table 2) indicate a bound interaction producing a stabilisation effect. In fact, the computed O2...O3 bond length is 2.397 Å, a distance which is shorter than twice the oxygen atom van der Waals radius (1.40 Å).<sup>[45]</sup> This kind of oxygen–oxygen interaction, having a stabilization character, has been recently reported in the literature.<sup>[46, 47]</sup> The interactions pointed out in complex **7** are also clearly reflected in the corresponding geometrical parameters showed in Figure 2. This is the complex having the smallest hydrogen bond distance (1.740 Å) and accordingly, the values of  $\rho = 0.0409 \text{ a.u.}$  and  $\nabla^2\rho = 0.1222 \text{ a.u.}$  at the corresponding bcp are the largest (see Table 2). The geometrical changes induced by the complex interaction are a lengthening of the C=O bond distance by 0.017 Å, a shortening of the C–O bond length by 0.030 Å, and a lengthening of the O–H bond distance of formic acid by 0.023 Å, while the change in the radical hydroxyl bond length is much smaller. The computed stability for complex **7** is  $-2.98 \text{ kcal mol}^{-1}$  ( $\Delta H$  value) at CCSD(T) level of theory, although the B3LYP method predicts this complex more stable ( $\Delta H = -5.54 \text{ kcal mol}^{-1}$ , see Table 2). At this point it should be pointed out that complex **7** has been obtained only at the B3LYP level of theory. Any attempt to find it at MP2 or QCISD levels of theory has failed because at these levels complex **7** is less stable than complex **5** and the variational process in the geometry optimization produces an orbital rotation leading to the most stable complex **5**.

The different interaction types occurring in complexes **5** and **7** are clearly visualised in Figure 3, which shows the electron density difference map. Figure 3a corresponds to complex **5** and



**Figure 4.** Selected geometrical parameters of the optimized geometries obtained at B3LYP/6-311 + G(2df,2p) and QCISD/6-311 + G(2df,2p) in parentheses, for complexes formed between anti-HCOOH and OH. Distances are given in Ångstroms and angles in degrees.

displays the typical electron redistribution originated by the two hydrogen bonds. It presents a decreased electron density over the two interacting hydrogen atoms and an increased electron density over the two acceptor oxygen atoms, being these features similar to those reported recently for the  $\text{HO}_2\text{-H}_2\text{SO}_4$  complex.<sup>[48]</sup> On the other side, Figure 3b shows the electron redistribution in complex 7. In the region of the  $\text{C-O-H}\cdots\text{O-H}$  hydrogen bridge there is reflected a depleted electron density over the hydrogen and an increased electron density over the oxygen, which is typical of the  $\text{H}\cdots\text{O}$  hydrogen bond as discussed above. However, the  $\text{C=O}\cdots\text{O-H}$  interaction pointed out above by the topological properties of the wave function originates a decrease of the electron density over the oxygen of the carbonyl group, which faces with a decreased electron density in the hydroxyl radical (see the opposite side of the hydroxyl radical in Figure 2b, remind that complex 7 is not planar).

The last complex found with a cyclic structure corresponds to 8, which is a planar five-membered ring of  $\sigma$  symmetry ( $^2A'$ ) and presents the largest hydrogen bond lengths (2.459 and 2.268 Å at B3LYP level of theory, or 2.460 and 2.339 Å obtained using the QCISD approach. See Figure 2). The topological parameters of the wave function in Table 2 show the existence of two hydrogen bridges and a bcp of the ring type. The values of  $\rho$  and  $\nabla^2\rho$  at the H2O3 bcp are 0.0125 a.u. and 0.0471 a.u. respectively, while the corresponding values for the H3O1 bcp are  $\rho = 0.0095$  a.u. and  $\nabla^2\rho = 0.0361$  a.u., see Table 2. Moreover, the electron density difference map displayed in Figure 3c shows typical features of hydrogen bond as discussed above. Another point of interest concerning complex 8 is associated with its symmetry ( $A'$  or  $\sigma$  type). The unpaired electron of the OH moiety (O3) lies in the molecular plane and occupies an orbital which is mainly directed to the hydrogen of the formyl group (H2, see Figure 2). Therefore the H2O3 interaction could be better classified as a van der Waals rather than a hydrogen bond interaction. The geometric van der Waals restriction imposed by the five membered ring imply that this is the less stable complex ( $\Delta H = -0.81$  kcal mol $^{-1}$ ).

Finally, we have also found a further stationary point 9 (Figure 2), which has  $\pi$  symmetry ( $^2A''$ ). However this is not a true minimum but corresponds to a transition state resulting from a rotation through the  $\text{H1}\cdots\text{O3}$  axis in complex 5.

A further interesting point regarding the syn-HCOOH plus OH complexes refers the charge transfer between both moieties in the complex formation. In this context it is worth to remind the reader that the direction of the electron transfer is reverse to the direction of proton donation. The corresponding NBO computed values ( $\Delta q$  over the HCOOH) displayed in Table 2 show a net electron transfer over the OH radical except for compound 5, having a net electron transfer from OH to the formic acid. Thus, HCOOH can act both as Lewis acid as well as Lewis base in relation to the OH radical, depending on the way how OH approaches formic acid. The magnitude of the computed charge transfer ranges from 6.8 me (compound 3) to the very large 101.2 me (compound 7). The positive values of the  $\Delta q$  in complexes 1, 2, 3, and 4 indicate that in these cases HCOOH acts as a Lewis base and therefore it is expected that these complexes don't play any role in a gas phase process involving a proton abstraction by OH. This fact is particularly clear, looking at

the geometrical structure of these complexes, where the hydroxyl radical acts as a donor.

On the other side Table 2 shows that complex **5** has a  $\Delta q$  of  $-11.7$  me, pointing out that HCOOH acts as a Lewis acid. As shown above, complex **5** has two hydrogen bridges and there is a double charge transfer, from the HCOOH to OH and from OH to HCOOH, respectively. Please remind that the electronic structure of this complex ( $^2A''$ , see Figure 2 and above) indicates that the unpaired electron lies in a plane perpendicular to the molecular plane and the two hydrogen bonds take place between the lone pairs of the hydroxyl and carbonyl groups in the acceptor side. Thus, this double charge transfer suggests that this complex plays a role in a process involving a double proton transfer.<sup>[28]</sup> For complex **7** we have computed an unexpected very large  $\Delta q$  (101.2 me). This can be qualitatively understood on the basis of the above discussed O...O interaction, which favours a charge shift towards the hydroxyl radical. This complex plays also an important role in the atmospheric formic acid oxidation process by OH.<sup>[28]</sup> Finally, the computed  $\Delta q$  for complex **8** is 24.7 me, which, together with their structure displayed in Figure 2 indicates that this complex plays a role in the carboxylic hydrogen abstraction process by OH.<sup>[28]</sup>

## Complexes Formed between anti-HCOOH and OH

Regarding to the complexes formed between anti-HCOOH and OH, Figure 4 shows that all stationary points found in the present investigation are planar and possess a single hydrogen bond. As pointed out in the previous section, each complex is classified as  $A'$  or  $A''$ , according to the orientation of the unpaired electron of the radical.

Complexes **10**( $^2A'$ ), **12**( $^2A'$ ), **11**( $^2A''$ ), and **13**( $^2A''$ ) have the same interaction but different orientation. The acceptor is the oxygen of the carbonyl group while the OH radical acts as a donor. These

structures present the same kind of interaction than complexes **1** and **2** described above and accordingly, all their features are very similar. The hydrogen bond lengths range among 1.93 and 1.97 Å and their stability ( $\Delta H$ , see Table 3) range among  $-3.28$  and  $-3.61$  kcal mol $^{-1}$ . The topological parameters of the wave function, displayed in Table 4, are also very similar and compare with those of complexes **1** and **2** (see Table 2). In complexes **14**( $^2A'$ ) and **15**( $^2A''$ ) the acceptor group is the hydroxyl of formic acid as in complexes **3** and **4** discussed above and consequently they present very similar features. The computed hydrogen bond lengths are 2.138 and 2.082 Å respectively, and their stability ( $\Delta H$ ) is about  $-2.1$  kcal mol $^{-1}$ .

On the other side, complexes **16** and **17** are both  $^2A''$  having the same interaction, where the OH of the formic acid acts as a donor and the hydroxyl of the OH radical is the acceptor group. They correspond to different conformers which differentiate from each other by a rotation through the H1O3 axis. Therefore their hydrogen bond lengths (1.955 and 1.931 Å), their stability ( $\Delta H = -3.19$  and  $-3.82$  kcal mol $^{-1}$ ), and their topological values at the bcp ( $\rho = 0.0231$  and  $0.0254$  a.u. and  $\nabla^2\rho = 0.0785$  and  $0.0828$  a.u., respectively), are also very close to each other. Finally, it is worth to point out that the stability of these complexes are larger than the stability of complexes **3**, **4**, **14**, and **15** and therefore the OH radical is a better acceptor than the hydroxyl group of formic acid.

## Vibrational Frequencies

An important feature of hydrogen bonds concerns the vibrational spectrum. For conventional hydrogen bonds, the O–H stretch is red-shifted in an amount depending on the strength of the hydrogen bond, and their intensity is enhanced according to the changes of the associated dipole moments. In order to help possible experimental work in identifying these complexes, we have included in Table 5 the computed harmonic vibrational

**Table 5.** Frequencies (in cm $^{-1}$ ) scaled by the factor 0.9614<sup>[48]</sup> and intensities (in km mol $^{-1}$ ) for some selected vibrational modes.

Compound		Stretching mode OH (radical)		Stretching mode OH (HCOOH)		HOC out-of-plane wagging mode	
		Freq. <sup>[a]</sup>	Int. <sup>[b]</sup>	Freq. <sup>[a]</sup>	Int. <sup>[b]</sup>	Freq. <sup>[a]</sup>	Int. <sup>[b]</sup>
syn-HCOOH OH	$^1A'$	–	–	3590.1	63.0	649.3	145.7
	$2\Pi$	3571.1	14.9	–	–	–	–
<b>1</b>	$2A'$	3454.7 (–116.4)	367.7 (24.7)	3586.6 (–3.5)	74.4 (1.2)	659.9 (10.7)	155.1 (1.1)
<b>2</b>	$2A''$	3429.5 (–141.6)	379.7 (25.5)	3586.1 (–4.0)	74.4 (1.2)	662.5 (13.2)	152.6 (1.0)
<b>3</b>	$2A'$	3511.9 (–59.1)	206.2 (13.8)	3585.4 (–4.7)	73.1 (1.2)	632.4 (–16.9)	161.3 (1.1)
<b>4</b>	$2A''$	3510.9 (–60.1)	226.6 (15.2)	3586.4 (–3.7)	74.5 (1.2)	637.7 (–11.6)	159.8 (1.1)
<b>5</b>	$2A''$	3320.3 (–250.8)	48.3 (3.2)	3381.2 (–208.9)	590.9 (9.4)	737.6 (88.3)	142.5 (1.0)
<b>7</b>	$2A$	3618.7 (47.7)	61.4 (4.1)	3156.2 (–433.9)	143.6 (2.3)	899.9 (250.6)	114.7 (0.8)
<b>8</b>	$2A'$	3570.5 (–0.5)	21.5 (1.4)	3589.1 (–1.0)	74.9 (1.2)	633.4 (–15.8)	146.8 (1.0)
anti-HCOOH	$1A'$	–	–	3654.1	61.0	512.1	87.1
	$2A'$	3451.0 (–120.1)	363.2 (24.4)	3654.7 (0.6)	78.8 (1.3)	527.6 (15.6)	107.4 (1.2)
	$2A''$	3415.3 (–155.8)	347.6 (23.3)	3655.2 (1.1)	80.8 (1.3)	533.4 (21.4)	91.5 (1.1)
	$2A'$	3458.2 (–112.9)	343.0 (23.0)	3654.6 (0.4)	80.2 (1.3)	526.0 (14.0)	31.5 (0.4)
	$2A''$	3459.8 (–111.3)	337.5 (22.6)	3654.6 (0.5)	80.7 (1.3)	526.8 (14.7)	76.9 (0.9)
	$2A'$	3530.0 (–41.1)	157.1 (10.5)	3650.2 (–3.9)	75.0 (1.2)	489.0 (–23.0)	88.2 (1.0)
	$2A''$	3518.6 (–52.5)	184.6 (12.4)	3649.1 (–5.0)	75.6 (1.2)	503.3 (–8.7)	102.9 (1.2)
	$2A''$	3563.4 (–7.6)	22.9 (1.5)	3526.0 (–128.1)	459.2 (7.5)	631.1 (119.1)	104.1 (1.2)
	$2A''$	3557.8 (–13.2)	26.3 (1.8)	3502.0 (–152.1)	511.1 (8.4)	632.0 (120.0)	114.5 (1.3)

[a] Numbers in parentheses are frequency shifts relative to monomers. [b] Numbers in parentheses are the ratios between the intensity of the complex and the corresponding in the monomer.

frequencies corresponding to the two O–H stretching modes and the HOC out-of-plane wagging mode, for all the HCOOH...OH complexes. The frequencies have been scaled by the factor 0.9614 in order to correct for the anharmonic effects.<sup>[49]</sup> Included in Table 5 are also the frequency shifts, the intensity of each mode, and the ratios for the calculated intensities of the complex relative to the monomers. The frequency shifts have been calculated taking the difference between the vibrational frequency of the complex and the corresponding frequency in the isolated HCOOH or OH molecule.

Complexes **1–4** have a single hydrogen bridge and, according to their stability, our calculations predict shifts among 59 and 142 cm<sup>−1</sup> for the hydroxyl stretching mode of OH radical, while the corresponding intensities are enhanced by a factor among 26 and 14.

More interestingly are the vibrational changes produced in complexes **5** and **7**. Complex **5** has two hydrogen bonds involving the two hydroxyl groups and, as a consequence of this, our calculations predict the two OH stretching modes are red-shifted by 251 and 209 cm<sup>−1</sup> and the corresponding intensities are enhanced by the factors 3.2 and 9.4.

Complex **7** has one hydrogen bridge and one O...O interaction forming a five-membered ring. For this compound, we have calculated the largest red-shift in the OH stretching mode, which corresponds to the formic acid (433.9 cm<sup>−1</sup>), and an increase in the relative intensity by a factor of 2.3. Moreover it is also worth to point out in this case, a predicted blue shift by 250.6 cm<sup>−1</sup> for the HOC wagging mode (see Table 5), while the radical OH stretching mode is unshifted. These different features between the predicted spectra of **5** and **7** will allow identifying easily both complexes.

For complexes **10–17**, having a single hydrogen bond, we have calculated red-shifts among 53 and 156 cm<sup>−1</sup> in the corresponding OH stretching mode, depending also on their stability. The associated intensities are enhanced by a factor among 2 and 24.

## Conclusion

The structure, stability, and electronic features of seven hydrogen bond complexes between syn-HCOOH and OH radical and eight hydrogen bond complexes between anti-HCOOH and OH radical is reported. All but one structures are planar, so that each complex can be classified as <sup>2</sup>A' or <sup>2</sup>A'', depending on the symmetry of the orbital in which the unpaired electron resides.

All complexes possessing the same kind of donor–acceptor interactions have very similar features, such as hydrogen bond distances and stabilities. Complexes **1**, **2**, **10**, **11**, **12**, and **13** present a (OH)HC=O...H–O hydrogen bond interaction and possess similar hydrogen bond distances (among 1.929 and 1.973 Å) and similar stabilities ( $\Delta H(298\text{ K})$  among −3.14 and −3.61 kcal mol<sup>−1</sup>). Complexes **3**, **4**, **14**, and **15** present a (O)HC(HO)...H–O hydrogen bond interaction and possess a larger hydrogen bond distance (among 2.035 and 2.138 Å) and a smaller stability ( $\Delta H(298\text{ K})$  among −1.28 and −2.12 kcal mol<sup>−1</sup>), pointing out the worse acceptor character of the hydroxyl group of formic acid. Complexes **16** and **17** present a single

(O)HCO–H...O–H interaction with bond distances 1.955 and 1.931 Å and similar stabilities ( $\Delta H(298\text{ K}) = -3.19$  and  $-3.82$  kcal mol<sup>−1</sup>, respectively), indicating that OH radical is a better acceptor group than the hydroxyl group of formic acid.

In addition we have found three complexes (**5**, **7**, and **8**) having a cyclic structure with multiple interactions. Complex **5** is a planar six-membered ring of A'' symmetry, where the unpaired electron resides in an orbital perpendicular to the molecular plane. This electronic distribution propitiates that both moieties (HCOOH and OH) act as donor and acceptor simultaneously, so that a cooperative effect is envisaged, enhancing thus its stability. Indeed this is the most stable complex ( $\Delta H = -5.96$  kcal mol<sup>−1</sup>). Complex **7** has a very interesting five-membered ring structure and is the only complex that has C<sub>1</sub> symmetry. The topological analysis of their wave function points out the existence of a single hydrogen bond, but it also indicates a slightly stabilizing O...O interaction between the oxygen of the hydroxyl radical and the oxygen of the carbonyl group of formic acid. This particular electronic feature propitiates that complex **7** has the shortest hydrogen bond length (1.740 Å), despite the geometrical restrictions imposed by its five-membered ring structure.

Interesting is the fact that the charge-transfer estimation, based on the NBO analysis, indicates that HCOOH can act as Lewis acid as well as Lewis basis with respect to the OH radical, depending on the way how OH approaches formic acid.

The computed red-shifts in the O–H vibrational stretching modes, originated by the complex formation are also reported and range among 40 and 434 cm<sup>−1</sup>, depending on the stability of the corresponding complex.

From a computational point of view, it is also of interest to indicate that the geometrical parameters obtained at B3LYP level of theory agree very well with those optimized using the computationally more demanding QCISD approach.

Supporting information: This material contains the Cartesian coordinates, absolute energies, enthalpies, harmonic vibrational frequencies, and dipole moments computed for all stationary points reported herein.

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