Structures of Carbonato and Bicarbonato Complexes of Bis(1,10-phenanthroline)Zinc(II): Experiment and Theory

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We report experimental and theoretical studies on the structure and properties of carbonato and bicarbonato complexes of bis(1,10-phenanthroline)zinc(II). The complex [Zn(phen)$_2$-O$_2$CO] has been synthesized and DFT calculations have been performed based upon its X-ray structure. The carbonate ligand coordinates in a bidentate binding mode to the metal centre with Zn–O distances of 2.130 and 2.092 Å in the X-ray structure and 2.027 Å for both distances in the calculated gas-phase structure. Because of the fundamental role of (bicarbonato)Zn^{II} complexes, especially in different carbonic anhydrases, the structures and properties of the experimentally unknown bicarbonato complexes of this kind were investigated using DFT with different basis sets up to the Ahlrichs triple zeta basis set with additional polarization functions. The bidentate bicarbonato complex [Zn(phen)$_2$O$_2$C(OH)]$^+$ was found to be about 8.2 kcal·mol^{-1} (SHAsvp), 6.4 kcal·mol^{-1} (Ahlrichs triple zeta with polarization functions) and 3.5 kcal·mol^{-1} (Ahlrichs triple zeta) more stable than the quasi-monodentate bicarbonato complex [Zn(phen)$_2$O(OH)CO]$^+$.
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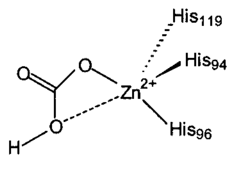
Introduction

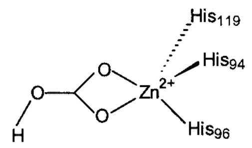
Knowledge of the structures of bicarbonato complexes of Zn^{II} is essential to understand the mechanism of human carbonic anhydrase (HCA),[1−12] an enzyme that catalyzes the hydration of CO_2 and dehydration of HCO_3^- according to the overall reaction given in Equation (1).

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \quad (1)$$

Two contrasting structural types have been proposed for these important bicarbonato complexes. The Lindskog structure involves a characteristic monodentate bicarbonate binding mode, i.e., one of the carboxylate oxygen atoms is bound to the zinc ion, whereas the hydroxy oxygen atom is only weakly coordinated to the metal centre. The Lipscomb structure involves a characteristic bidentate bicarbonate binding mode, i.e., both the carboxylate oxygen atoms are utilized as ligands for the zinc centre.[10−12] Two X-ray structures involving monodentate bicarbonate binding to different carbonic anhydrases, i.e. a bicarbonate-HCAI intermediate and a mutant intermediate of bicarbonate-HCAII (Thr-200→His-200), have been determined and taken to support the Lindskog structure.[13,14] However, calculations suggest that the bidentate coordination mode of bicarbonate contributes significantly towards the effective catalytic activity of the enzymes.[15,16] The structure of bicarbonate bound to Co^{II}-substituted carbonic anhydrase closely resembles the bidentate Lipscomb bicarbonate structure with the two bicarbonate oxygen atoms at between 2.3 and 2.5 Å from the Co^{II} ion.[17] However, bicarbonato complexes of Zn^{II} are unstable and have only recently be identified structurally.[18−23]



Lindskog structure



Lipscomb structure

To gain more insight into the possible coordination geometries of bicarbonate to related metal centres, we recently isolated and characterized the first stable bicarbonato complexes of bis(1,10-phenanthroline)copper(II).[24] Two complexes of the type [Cu(phen)$_2$OCO$_2$H]ClO$_4$ and [Cu(phen)$_2$-O$_2$COH]ClO$_4$, in which bicarbonate is bound in monodentate and bidentate modes, respectively, could be characterized (Figure 1). The structures reported resemble

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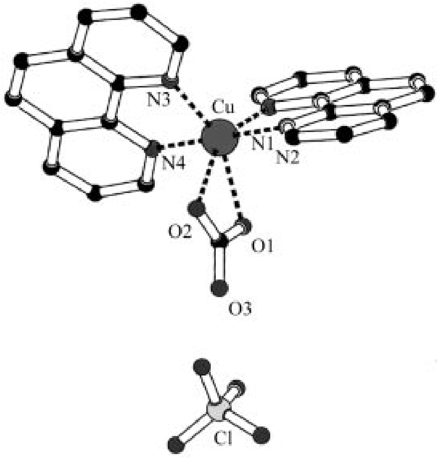
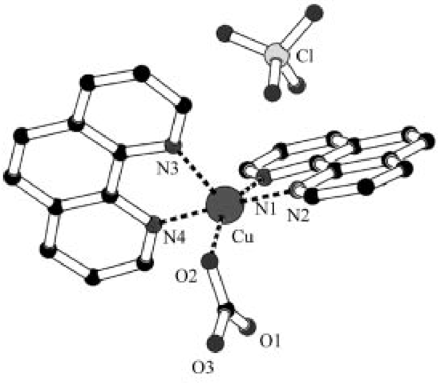


[Cu(phen)$_2$O$_2$COH]ClO$_4$



[Cu(phen)$_2$OCO$_2$H]ClO$_4$

Figure 1. X-ray structure of the two Cu(phen)$_2$ bicarbonate complexes

Lipscomb- and Lindskog-like intermediates closely with respect to the coordination mode of bicarbonate, but not with respect to the coordination geometry of the metal centre.

We could not isolate similar bicarbonato complexes of Zn^{II}, obtaining instead only [Zn(phen)$_2$O$_2$CO] under all experimental conditions. In this structure, carbonate is bound in a bidentate mode − structural details are reported here. Therefore, we have used density functional theory (DFT) to calculate the structures and stabilities of the two possible bicarbonato complexes of Zn^{II}.

Results and Discussion

[Zn(phen)$_2$(CO$_3$)]·7H$_2$O (1)

Table 1. Selected bond lengths [Å] and angles [°] for [Zn(phen)$_2$(CO$_3$)]·7H$_2$O (**1**)

Zn−O(2)	2.091(2)	Zn−O(1)	2.129(2)
Zn−N(3)	2.144(2)	Zn−N(1)	2.154(2)
Zn−N(2)	2.160(2)	Zn−N(4)	2.187(2)
C(25)−O(3)	1.254(3)	C(25)−O(1)	1.296(3)
C(25)−O(2)	1.293(3)		
O(2)−Zn−O(1)	62.15(7)	O(2)−Zn−N(3)	99.14(7)
O(1)−Zn−N(3)	94.29(7)	O(2)−Zn−N(1)	92.96(7)
O(1)−Zn−N(1)	97.89(7)	N(3)−Zn−N(1)	165.82(7)
O(2)−Zn−N(2)	149.36(7)	O(1)−Zn−N(2)	89.91(7)
N(3)−Zn−N(2)	95.01(7)	N(1)−Zn−N(2)	77.85(7)
O(2)−Zn−N(4)	106.16(7)	O(1)−Zn−N(4)	164.40(7)
N(3)−Zn−N(4)	76.78(7)	N(1)−Zn−N(4)	92.83(7)
N(2)−Zn−N(4)	103.46(7)	O(3)−C(25)−O(1)	121.8(2)
O(3)−C(25)−O(2)	123.6(2)	O(1)−C(25)−O(2)	114.6(2)

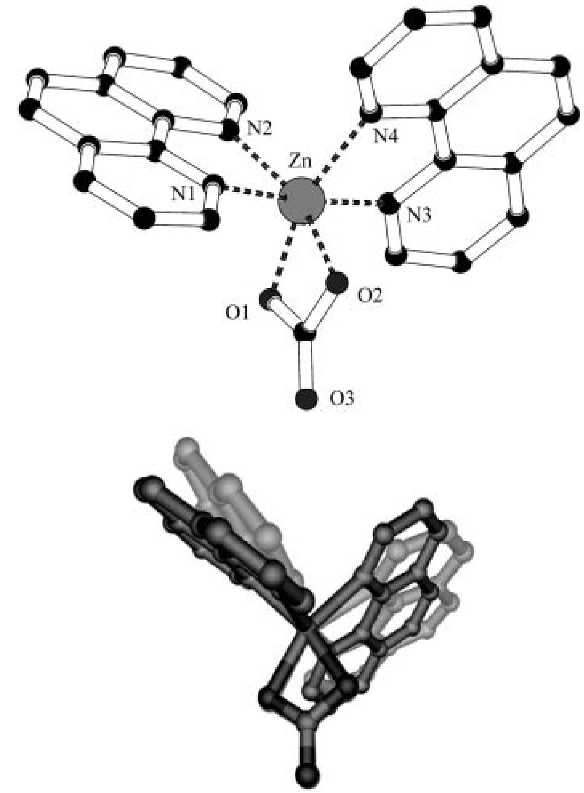


Figure 2. X-ray structure (top) and calculated structure (superimposed on the X-ray structure, bottom) of the [Zn(phen)$_2$(O$_2$CO)] complex

Structural and crystallographic data for this complex are reported in Tables 1 and 7. Figure 2 shows that the N$_4$-coordinated Zn^{II} ion is coordinated by carbonate in a bidentate mode. The bond lengths for Zn−O1 and Zn−O2 are 2.129(2) and 2.091(2) Å, respectively. The coordination polyhedron of the zinc atom can be described as a distorted octahedron. By comparison, in [Cu(phen)$_2$(CO$_3$)]·7H$_2$O the Cu−O1 and Cu−O2 bond lengths are 2.421(3) and 1.972(3) Å, respectively,[25] i.e. the carbonate ligand forms a stronger bidentate coordination mode in the Zn^{II} complex than in the corresponding Cu^{II} complex. This behaviour differs from that in monodentate-coordinated nitrate or binuclear carbonate complexes of Zn^{II} reported before.[21,26] Therefore, the bidentate distortion of bicarbonate/carbonate Zn^{II}/Cu^{II} complexes is not only determined by the metal centre, but also by the geometry of the metal complexes.

^{13}C NMR Spectra

^{13}C NMR spectra of the labelled complex **1** were recorded in C_2D_5OD. The $[Zn(phen)_2{}^{13}CO_3]\cdot 7H_2O$ complex revealed a medium peak at $\delta = 171.1$ ppm for the bidentate binding of the carbonate group and a strong peak at $\delta = 163.3$ ppm for free HCO_3^-. Due to the low solubility of complex **1** in water, ^{13}C NMR spectra of 10 mM $[Zn(phen)_2(H_2O)](NO_3)_2$ in the presence of 30 mM $NaH^{13}CO_3$ were also recorded in D_2O/[D_6]DMSO (1:1). The spectra revealed a weak multiplet peak at $\delta = 167.5-171.1$ ppm for the various binding forms of the carbonate group, i.e. polynuclear carbonato complexes, a strong peak at $\delta = 161.5$ ppm for free HCO_3^- and a medium peak at $\delta = 126.4$ ppm for free CO_2. The chemical shift for the bidentate carbonate group lies within the values reported for other (carbonato)zinc complexes.[21,27,28]

Computational Details

Calculations were performed using the Gaussian98[29] program package with the B3LYP[30-32] combination of functionals and both the Schäfer, Horn, Ahlrichs split valence (SHAsv)[33] and the Ahlrichs triple zeta basis sets.[34] These levels of theory are referred to as B3LYP/SHAsv and B3LYP/Ahlrichs_tz, respectively. Calculations with additional polarization functions,[35,36] referred to as SHAsvp and Ahlrichs_tzp, respectively, were also performed. The latter is the highest level of theory used in this study. Due to the large number of basis functions, the use of these basis sets was restricted to the centres of interest, viz. the Zn^{2+} centre, the carbonate ligand and the N atoms of the phenanthroline ligands. For the remaining atoms of the phenanthroline chelates, the SHAsv basis set was used. The following discussion is based on the highest level of calculations, except where stated mentioned. Minimizations used the Berny algorithm along with redundant internal coordinates.[37,38] All structures were verified as local minima on the potential energy hypersurface by frequency analyses, and the zero-point vibrational energies obtained were used unscaled to correct the total energies. The DFT calculations started with the X-ray structure of the $[Zn(phen)_2(CO_3)]$ complex as shown in Figure 2. All geometries of the complexes $[Zn(phen)_2O_2CO]$, $[Zn(phen)_2O(OH)CO]^+$, and $[Zn(phen)_2O_2COH]^+$ were fully optimized without any constraints.

The structure for the carbonate complex was first calculated in C_1 symmetry corresponding to the original X-ray data, followed by further optimization in C_2 symmetry

Table 2. Energies and properties of the calculated structures

		$[Zn(phen)_2O_2CO]$	$[Zn(phen)_2O_2CO]$	$[Zn(phen)_2O_2COH]^+$	$[Zn(phen)_2O(OH)CO]^+$	$[Zn(phen)_2O(OH)CO]^{+\#}$
Basis set	Point group	C_1	C_2	C_1	C_1	C_1
	NImag[a]	0	0	0	0	1
SHAsv	E_{abs}[b]	−3184.843960	−3184.843941	−3185.323211	−3185.340750	–
	ZPE[c]	228.9	228.9	237.7	236.8	–
	E_{rel}[d]	–	–	11.9	0	–
SHAsvp	E_{abs}[b]]	–	−3185.225639	−3185.705204	−3185.691203	−3185.645361
	ZPE[c]	–	227.3	236.1	235.6	233.0
	E_{rel}[d]	–	–	0	8.2	37.6
Ahlrichs_tz[e]	E_{abs}[b]	–	−3186.561845	−3187.032820	−3187.028006	–
	ZPE[c]	–	226.1	235.2	234.7	–
	E_{rel}[d]	–	–	0	3.5	–
Ahlrichs_tzp[f]	E_{abs}[b]	−3185.470208	–	−3185.945652	−3185.935461	–
	ZPE[c]	228.9	–	237.5	237.1	–
	E_{rel}[d]	–	–	0	6.4	–

[a] Number of imaginary frequencies (0 for ground states, 1 for transition states). [b] Absolute energy [hartree]. [c] Zero point energy [kcal·mol^{-1}]. [d] Difference in energy between the two bicarbonate complexes [kcal·mol^{-1}]. [e] 6-31G for H (not included in this basis set). [f] SHAsv for C,H (phenanthrolines).

Table 3. Comparision of the X-ray and calculated bond lengths with different basis sets for $[Zn(phen)_2O_2CO]$

Method	C−O3	C−O1	C−O2	Zn−O1	Zn−O2	Zn−N1	Zn−N2	Zn−N3	Zn−N4
X-ray	1.252	1.289	1.296	2.130	2.092	2.146	2.158	2.156	2.189
SHAsv	1.252	1.369	1.369	2.041	2.041	2.147	2.211	2.147	2.211
SHAsvp	1.224	1.345	1.345	2.004	2.004	2.201	2.380	2.201	2.380
Ahlrichs_tz[a]	1.250	1.369	1.369	2.051	2.051	2.184	2.240	2.184	2.240
Ahlrichs_tzp[b]	1.231	1.340	1.341	2.027	2.027	2.185	2.277	2.185	2.278
SHAsvp $[Zn(phen)_2O_2CO] + 2\ H_2O$	1.228	1.338	1.338	2.024	2.024	2.239	2.268	2.239	2.268

[a] 6-31G for H (not included in this basis set). [b] SHAsv for C,H (phenanthrolines).

(SHAsv). Both structures were verified as local minima, and were found to be very similar and practically of the same energy (Table 2). However, the structure with C_2 symmetry was used as the starting structure for the higher level calculations. All calculations were performed for the gas phase, and therefore neither solvent nor crystal effects, nor the influence of counterions was considered. As expected for a molecule in two different states of aggregation, this results in minor structural differences between the calculated and X-ray structures of the unprotonated carbonate complex. Thus, in the calculated structure the carbonate ligand is 0.068 Å closer to the metal centre with a Zn−C distance of 2.437 Å, and the calculated bond lengths for Zn−O1 and Zn−O2 of 2.027 Å are about 0.065 and 0.103 Å shorter than the corresponding bond lengths of 2.092 and 2.130 Å, respectively, found in the X-ray structure. The calculated angle for O1−C−O2 of 112.5° is 2.1° smaller, whereas the O1−Zn−O2 angle is 4.6° larger than in the X-ray structure, viz. 66.7° compared with 62.1°. The C−O1 and C−O2 distances were calculated to be 1.340 and 1.341 Å, respectively, i.e. 0.051 and 0.045 Å longer than in the X-ray structure. A comparison of selected bond lengths from the X-ray and theoretical structures is given in Table 3.

The arrangement of the coordinated phenanthroline ligands depends on the solid or gas phase state of the complex. The dihedral angle between the two ring systems decreases from 125.4° in the crystal to 113.5° in the gas phase structure owing to the more ordered and stacking arrangement of the ligands and the presence of seven water molecules in the crystal structure. Consideration of the two water molecules near the carbonate ligand in the calculations (see below) leads to an almost unchanged dihedral angle of 113.6°. The calculated Zn−N distances show two short Zn−N(1) and Zn−N(3) bonds of 2.185 Å for each, and two long bonds for Zn−N(2) and Zn−N(4) of 2.277 and 2.278 Å. In the X-ray structure a short bond [Zn−N(1) = 2.146 Å] and a long one [Zn−N(4) = 2.189 Å] and two almost equal [Zn−N(2,3) ≈ 2.157 Å] bond lengths for the phenanthroline ligands were found.

In this study the importance of the selected basis set on the bond lengths, especially for Zn^{2+}, could be confirmed. As shown in Table 3, for both basis sets the best agreement between X-ray and calculated structures was obtained without adding additional polarization functions to these basis sets. This paradoxically suggests that these basis sets give larger errors because they cannot reproduce the differences between gas phase and solid state structures. The calculations with the SHAsvp basis set lead to a shortening of between 0.02 and 0.03 Å of all bonds in which O atoms are involved. The corresponding effect on the Zn−N distances is more distinctive. The Zn−N2/N4 bond length is enlarged from 2.211 to 2.380 Å. Thus, with this basis set, the coordination sphere for Zn is strongly distorted in comparison with that found in the X-ray structure. This discrepancy did not occur with the Ahlrichs_tz basis set. The Zn−N bonds are found to be 2.184 and 2.240 Å. All C−O and Zn−O bonds are longer than the SHAsvp results, but almost identical to those found with SHAsv. We included two additional water molecules in our calculations to study their influence on the Zn−O bond lengths, which are too short for all basis sets used. The location of these water molecules was chosen according to the X-ray data. In the optimized structure (Figure 3) the O(carbonate)−O(water) distance averages as 2.643 and 2.648 Å. We used the SHAsvp basis set in a balance between accuracy and computational effort for the optimization. This was performed in C_1 symmetry without any constraints. Summarized bond lengths are given in Table 3. At this level of theory the Zn−O bond length was calculated to be 2.024 Å, which is 0.020 Å (1%) longer than in the corresponding structure without the water molecules. Transferred to the SHAsv and Ahlrichs_tz levels, an elongation of 1% means a Zn−O bond length of about 2.061 and 2.047 Å, respectively, and results in a slightly better agreement with the X-ray structure.

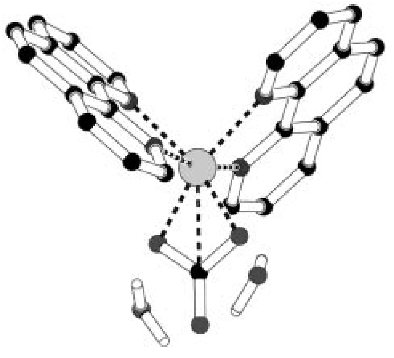


Figure 3. Calculated structure of $[Zn(phen)_2(O_2CO)]$ with two water molecules

The agreement between the X-ray and calculated Ahlrichs_tzp structure is such that the structures and relative energies of the bicarbonate complexes for which experimental data are not available can be satisfactorily calculated. The Lipscomb bicarbonate structure is represented in this model by protonation of O(3) and the Lindskog structure by protonation of O(1). The energies and properties of the calculated structures are summarized in Table 2.

The bicarbonate complex **A** clearly shows a bidentate binding mode with Zn−O bond lengths of 2.156 and 2.228 Å. The former is about 0.2 Å and the latter 0.13 Å shorter than in the related Cu complex,[24] and 0.129 and 0.201 Å, respectively, longer than in the Zn carbonate structure. The C−O(3) distance is elongated to 1.350 Å, whereas the C−O(1) and C−O(2) distances are shortened to 1.267 and 1.260 Å, respectively. As expected, the influence of protonation of O(3) on the structure of the phenanthroline ligands is small. All Zn−N bond lengths decrease to 2.159, 2.169, 2.158, and 2.166 Å, respectively, and the dihedral angle increases by 3.9° on protonation. The coordination sphere of the metal centre is best described as distorted octahedral (Figure 4). Structural details for the different basis sets are given in Table 4. The bicarbonate structure **A** was found to be the most stable bicarbonate complex. Its energy is about 8.2 kcal·mol^{-1} (SHAsvp), 3.5 kcal·mol^{-1} (Ahlrichs_tz) and 6.4 kcal·mol^{-1} (Ahlrichs_tzp) lower

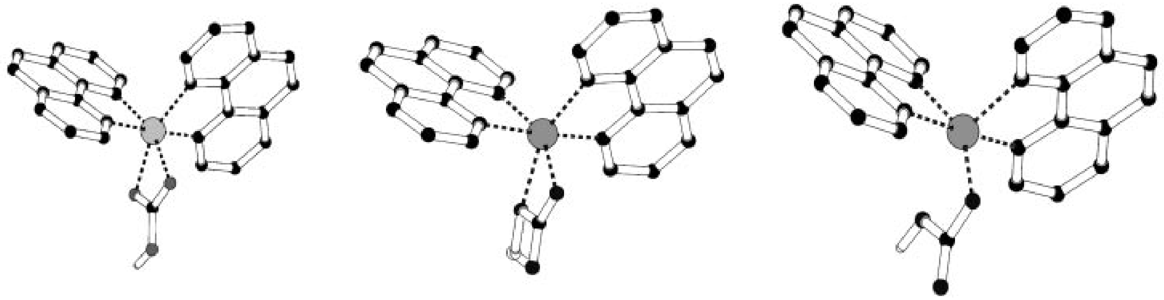


Figure 4. Structures of $[Zn(phen)_2O_2COH]^+$ (**A**), $[Zn(phen)_2O(O{\cdots}H)CO]^{+\#}$ (transition state for proton transfer), and $[Zn(phen)_2O(OH)CO]^+$ (**B**), respectively

than the bicarbonate complex with the proton bound to O(1) (Table 2).

In the calculated structure of **B**, a strong Zn−O(2) bond of 1.973 Å, which is only 0.051 Å shorter than the 2.024 Å in the bidentate bicarbonate structure, and a weak binding of O(1) to the metal centre with a Zn−O(1) bond length of 2.698 Å, were found. This is consistent with the calculation for the related copper complex (see below). Therefore, the binding mode has a somewhat bidentate character in comparison with the X-ray data of the analogous copper complex, which clearly binds the bicarbonate ligand in a monodentate binding mode. This behaviour shows a distinct dependence on the basis set. The Zn−O(1) distance varies from 2.542 Å (SHAsvp) to 2.980 Å (Ahlrichs_tz). The calculated C−O(1) bond length averages 1.421 Å, whereas the C−O(2) bond length averages 1.283 Å. In terms of the carbonate structure, the third C−O bond, C−O(3), remains, at 1.211 Å, almost unchanged. The structural changes on the phenanthroline ligands concern the Zn−N bond lengths, for which the values are between 2.121 and 2.177 Å, and the dihedral angle of 120.5° is 3.4 and 7.8° larger than in the bicarbonate **A** and in the carbonate structures, respectively. With the SHAsv basis set, in contrast to all other basis sets used, this bicarbonate structure was found to be lower in energy. However, this basis set gives acceptable structures, except for the Zn−O(1) distance, but the calculated energies must be treated with care. Structural details are given in Table 4.

Although, due to the significantly different coordination sphere, these complexes cannot be seen as model complexes for the active site of carbonic anhydrase, the energy of activation for the proton transfer reaction from O1 to O2 is of interest. It was possible to calculate the transition state for this reaction using the QST2 method. In the resulting structure the proton is located almost centrally between O1 and O3 with distances of 1.263 and 1.339 Å, respectively. The binding mode of the bicarbonate ligand changes from monodentate to more bidentate with Zn−O bond lengths of 2.054 and 2.409 Å, respectively. The C−O3 bond is shortened to 1.274 Å, whereas the C−O1 distance remains practically unchanged. Frequency analysis clearly shows a single imaginary frequency almost solely due to the displacement of the hydrogen atom. The activation energy for the proton transfer was calculated to be 37.6 $kcal{\cdot}mol^{-1}$, which is close to values found previously for the uncatalyzed proton transfer reactions in related Zn complexes.[39,40]

To validate the methods used here, additional calculations were performed on the related copper bicarbonate complexes for which X-ray data are available.[24] For the $[Cu(phen)_2O(OH)CO]^+$ complex, the structural agreement between experimental and theoretical data is similar to that for the $[Zn(phen)_2(O_2CO)]$ complex. The C−O1 and C−O2 bonds in the calculated structures, viz. 1.295 and 1.397 Å, respectively, are longer than in the X-ray structure (1.264 and 1.364 Å), and the C−O3 bond is 0.012 Å too long. The results for the Cu−O distances are somewhat different. The Cu−O2 bond was calculated to be 1.939 Å, which is 0.059 Å shorter than the X-ray data, but of the same order as found for all metal−O2 bond lengths calculated here for this type of complexes. It was therefore not surprising that the Cu−O1 bond was found to be significantly shorter, viz. 2.720 Å compared with 3.045 Å in the X-ray data, which is similar to the Zn−O1 distances in the $[Zn(phen)_2O(OH)CO]^+$ complex. As already mentioned, this effect depends strongly on the basis set employed. A summary of structural details is given in Table 5. Similar structural differences were obtained between gas phase and solid state structures for the $[Cu(phen)_2O_2COH]^+$ complex. The C_2 symmetry found in the X-ray data is lowered to C_1 in the calculated structure with bond lengths of 1.988 and 2.488 Å, respectively, in contrast to 2.359 Å for both bond lengths in the X-ray structure. In this case, an additional factor to the basis set effects mentioned above is the absence of the perchlorate anion in the calculations. In the X-ray structure, the ClO_4^- anion is positioned like a cap over the bicarbonate ligand with a distance of 2.575 Å between $O(HCO_3^-)$ and $O(ClO_4^-)$. This indicates two hydrogen bonds between the bicarbonate and the perchlorate ions, which leads to a more symmetric arrangement of the bicarbonate ligand with respect to the metal centre. All calculated C−O distances are elongated between 0.037 and 0.103 Å and the Cu−N bonds are in the range of 2.074, 2.098, 2.113, and 2.330 Å. The former values are significantly shorter than those found in the Zn complexes, whereas the last value has the same magnitude as found for the $[Zn(phen)_2(O_2CO)]$ complex (without considering the additional two water molecules). According to our calculations,

Table 4. Comparison of the calculated bond lengths with different basis sets for $[Zn(phen)_2O_2C(OH)]^+$ and $[Zn(phen)_2O(OH)CO]^+$

	$[Zn(phen)_2O_2C$-$(OH)]^+$	$[Zn(phen)_2O$-$(O\cdots H)CO]^+$ #	$[Zn(phen)_2O$-$(OH)CO]^+$
SHAsv:			
C−O3	1.366	−	1.230
C−O1	1.297	−	1.465
C−O2	1.285	−	1.304
Zn−O1	2.224	−	2.570
Zn−O2	2.174	−	1.994
Zn−N1	2.126	−	2.171
Zn−N2	2.152	−	2.151
Zn−N3	2.124	−	2.175
Zn−N4	2.152	−	2.183
O1−H	−	−	1.000
O3−H	0.986	−	−
SHAsvp:			
C−O3	1.341	1.274	1.206
C−O1	1.270	1.263	1.426
C−O2	1.262	1.261	1.286
Zn−O1	2.179	2.409	2.542
Zn−O2	2.135	2.054	1.964
Zn−N1	2.184	2.178	2.195
Zn−N2	2.212	2.194	2.165
Zn−N3	2.184	2.172	2.194
Zn−N4	2.212	2.177	2.194
O1−H	−	1.263	0.975
O3−H	0.974	1.339	−
Ahlrichs_tz:[a]			
C−O3	1.365	−	1.232
C−O1	1.284	−	1.442
C−O2	1.284	−	1.299
Zn−O1	2.322	−	2.980
Zn−O2	2.150	−	1.955
Zn−N1	2.151	−	2.172
Zn−N2	2.149	−	2.118
Zn−N3	2.149	−	2.169
Zn−N4	2.154	−	2.137
O1−H	−	−	0.983
O3−H	0.983	−	−
Ahlrichs_tzp:[b]			
C−O3	1.350	−	1.211
C−O1	1.267	−	1.421
C−O2	1.260	−	1.283
Zn−O1	2.228	−	2.698
Zn−O2	2.156	−	1.973
Zn−N1	2.159	−	2.174
Zn−N2	2.169	−	2.143
Zn−N3	2.158	−	2.177
Zn−N4	2.166	−	2.121
O1−H	−	−	0.977
O3−H	0.977	−	−

[a] 6-31G for H (not included in this basis set). [b] SHAsv for C,H (phenanthrolines).

Table 5. Comparison of the X-ray and calculated bond lengths with the SHAsvp basis set for the Cu bicarbonate complexes

	$[Cu(phen)_2O_2COH]^+$		$[Cu(phen)_2O(OH)CO]^+$	
	X-ray	calculated	X-ray	calculated
C−O3	1.243	1.346	1.197	1.209
C−O1	1.196	1.298	1.364	1.397
C−O2	1.196	1.233	1.264	1.295
Cu−O1	2.359	2.488	1.998	1.939
Cu−O2	2.359	1.988	3.045	2.720
Cu−N1	1.997	2.098	2.052	2.069
Cu−N2	2.119	2.330	1.987	2.122
Cu−N3	1.997	2.074	1.988	2.085
Cu−N4	2.119	2.113	2.173	2.293
O3−H	−	0.975	−	−
O1−H	−	−	−	0.976
Energies:				
E_{abs}[a]	−	−3046.805004	−	−3046.798996
ZPE[b]	−	236.1	−	235.8
E_{rel}[c]	−	0	−	3.8

[a] Absolute energy [hartree]. [b] Zero point energy [kcal·mol^{-1}]. [c] Difference in energy between the two bicarbonate complexes [kcal·mol^{-1}].

the $[Cu(phen)_2O_2COH]^+$ complex is about 3.8 kcal·mol^{-1} more stable than the corresponding $[Cu(phen)_2O(OH)CO]^+$ complex.

Based on the optimized structures obtained with the Ahlrichs_tzp basis set, the ^{13}C NMR shielding factors were calculated using the same basis set and compared with the experimental values obtained for complex **1**. The results (Table 6) demonstrate a good agreement between the experimental and theoretical values. The predicted values for the two bicarbonate complexes demonstrate that protonation of the chelated carbonate ligand (**A**) does not have a significant effect on the chemical shift, in contrast to the ring-opened protonated species (**B**). In fact, in the latter case the chemical shift is very close to that of uncoordinated bicarbonate, suggesting that the bicarbonate ligand is only weakly coordinated to the Zn centre.

The optimized theoretical structures clearly demonstrate the feasibility of stable bicarbonato complexes of bis(phenanthroline)zinc(II), even if these could not be isolated from solution. This, along with the recently identified structures of stable monodentate and bidentate (bicarbonato)Zn^{II} complexes[23] and the results of DFT studies for the conversion of carbon dioxide into bicarbonate with the $[(NH_3)_3Zn(OH)]^+$ model catalyst,[40,41] shows that stable bicarbonato complexes can form part of the overall catalytic cycle of carbonic anhydrase. According to our calculations the ring-closed complex **A** is 8.2 kcal·mol^{-1} (SHAsvp), 6.4 kcal·mol^{-1} (Ahlrichs_tzp), and 3.5 kcal·mol^{-1} (Ahlrichs_tz) more stable than the ring-opened complex **B**. This relatively small difference in energy is in good agreement with reactivity models for a series of zinc complexes.[41]

Experimental Section

$[Zn(phen)_2CO_3]\cdot 7H_2O$ (1): A mixture of (0.284 g, 0.5 mmol) of $[Zn(phen)_2(H_2O)](NO_3)_2$ and (0.336 g, 4.0 mmol) of $NaHCO_3$ was dissolved in 20 mL of water and stirred for 5 min at room temperature. The solution was filtered and allowed to stand in air for slow concentration. After a few days, colourless block crystals (0.212 g; 69.5%) suitable for X-ray analysis were obtained. IR cm^{-1} (KBr pressed pellet): $\tilde{\nu}$ = 1342 (s, CO_3^{2-}). $C_{25}H_{30}N_4O_{10}Zn$ (611.92): calcd. C 49.07, H 4.94, N 9.16; found C 49.05, H 4.88, N 8.96.

Table 6. NMR shielding values for the carbonate and bicarbonate ligands in the Zn phenanthroline complexes

	Calculated (absolute)[a] [ppm]	Calculated (relative to TMS)[a] [ppm]	Experimental [ppm]
TMS	183.3	–	0
[Zn(phen)$_2$O$_2$CO]	6.9	176.4	171.1
[Zn(phen)$_2$O$_2$COH]$^+$	8.6	174.7	–
[Zn(phen)$_2$O(OH)CO]$^+$	24.7	158.6	–
Free HCO$_3$$^-$	20.7	162.6	163.3

[a] Ahlrichs_tzp and SHAsv for C (phenanthrolines) and H.

Spectral Measurements: Infrared spectra were recorded with a Nicolet 5SX instrument using the KBr pellet method. ^{13}C NMR spectra were recorded with a Bruker DPX 300 MHz spectrometer.

X-ray Structure Analysis: Analyses on block single crystals of complex **1** were performed with a Philips PW1100/10 diffractometer. Intensity data were collected using the ω/2θ-scan technique and corrected for Lorentz and polarization effects. The structure of complex **1** was solved by direct methods using the SIR-92 program[42] and refined by full-matrix least-squares methods on F^2 using the SHELXL-93 program.[43] Hydrogen atoms were located partially from a difference synthesis and refined with an overall isotropic thermal parameter. Crystallographic data and data collection parameters are summarized in Table 7, and selected bond lengths and bond angles are given in Table 1. A labelled diagram of **1** is shown in Figure 2. CCDC-175269 for [Zn(phen)$_2$(CO$_3$)]·7H$_2$O (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

Table 7. Crystallographic details for complex **1**

Empirical formula	C$_{25}$H$_{30}$N$_4$O$_{10}$Zn
Formula mass	611.91
Temperature [K]	293(2)
Wavelength [Å]	0.71069
Space group	$P2_1/c$
a [Å]	9.937(3)
b [Å]	26.414(5)
c [Å]	10.571(3)
α [°]	90
β [°]	105.737(18)
γ [°]	90
V [Å^3]	2671(2)
Z	4
ρ(calcd.) [mg m^{-3}]	1.48
Abs. coeff. [m^{-1}]	0.975
F(000)	1216
Crystal size [mm]	0.68×0.55×0.40
θ range [°]	2.26−25.06
hkl ranges	−11/11, 0/31, −12/5
Reflections collected	6838
Independent reflections	4538
R(int)	0.082
Goodness of fit on F^2	1.03
R_1 [a]	0.066
wR_2[b]	0.153
Largest diff. peak [e·Å^{-3}]	−0.622, 0.53

[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2)^2]^{1/2}$.

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