A monoaqua zinc complex. Unique acid dissociation behaviour

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Using the 1 : 2 condensate of benzil dihydrazone and 2-acetylpyridine as the ligand L, two complexes of zinc, $[ZnL(CH_3COO)]PF_6$ (**1**) and $[ZnL(H_2O)ClO_4]ClO_4 \cdot H_2O$ (**2**), are synthesised from $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Zn(ClO_4)_2 \cdot 6H_2O$, respectively. From X-ray crystallography, both the complexes are found to be single helical with the metal in distorted octahedral N_4O_2 environment. In **1**, the two oxygen atoms come from the bidentate acetate while **2** is a monoaqua complex with a perchlorate anion bound to the metal in monodentate fashion. The perchlorate in **2** is not at all weakly bound [Zn–O(perchlorate) 2.256(4) Å]. Still in acetonitrile solution, the coordinated perchlorate ion dissociates upon deprotonation [reaction (i)].

$$[ZnL(H_2O)(ClO_4)]^+ \overset{K_a}{\rightleftharpoons} [ZnL(OH)]^+ + H^+ + ClO_4^- \quad (i)$$

This is supported by gas phase AM1 calculations. From solution conductivity, the pK_a value of reaction (i) is determined as 5.71 (±0.19). It is estimated that had **2** been soluble in water, it would have a pK_a value of ~2 in water. The cation $[ZnL(OH)]^+$ generated in reaction (i) could not be isolated in the solid state. From AM1 calculations, it is found to have a distorted tetrahedral ZnN_3O core. Complex **2** is ineffective in bringing about hydration of CO_2.

Introduction

Mononuclear zinc complexes containing a coordinated water molecule are important because of their relevance to carbonic anhydrases (CA),[1–3] zinc containing enzymes. The essential physiological function of CA is to catalyse the reversible hydration of CO_2 – reaction (1).

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

Its active site, as revealed by X-ray work, contains a pseudo-tetrahedral zinc center coordinated to three histidine (His) imidazole moieties and either a water molecule or a hydroxide ion depending on the pH. The acid dissociation constant pK_a of the coordinated water molecule in CA is around 7. Facile formation of the $(His)_3Zn(II)$–OH species under physiological conditions is the key to the activity of CA. From model studies on monoaqua zinc complexes of N donor ligands,[4,5] it emerges that the pK_a value of the water molecule bound to the zinc center depends on the coordination environment and charge on the complex. A general observation is that pK_a decreases with the decreasing coordination number and increasing positive charge. With certain counter-intuitive factors operating, it has not yet been possible to devise a monoaqua zinc complex of a N donor ligand with a pK_a value lower than 6.2.[5] In fact, at one time the main concern of the inorganic chemists was whether in such complexes a pK_a value as low as 7 can be achieved. We have obtained a monoaqua zinc complex of a N donor ligand that has a pK_a much less than 6. Its synthesis, X-ray crystal structure and some chemical properties are described here.

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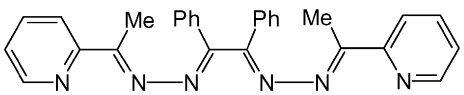
Results and discussion

The ligand L employed here is the 1 : 2 condensate of benzildihydrazone and 2-acetylpyridine.[6] Since the N–C–C–N dihedral angle in benzildihydrazone is ~70° in the solid state,[7] a Schiff base derived from it is expected to be helical. This is what is found in the X-ray crystal structure of L (Fig. 1). The helical twist is brought about mainly by the same torsion angle.



ligand L

Reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ with L in 1 : 1 molar proportion in methanol at room temperature and subsequent addition of 1 mol of NH_4PF_6 yields a yellow complex that analyses as $Zn(L)(CH_3COO)(PF_6)$ (**1**). On the other hand, by reacting $Zn(ClO_4)_2 \cdot 6H_2O$ with L in equimolar proportion in tetrahydrofuran at room temperature is obtained $Zn(L)(H_2O)_2(ClO_4)_2$ (**2**). The X-ray crystal structures of both the compounds **1** and **2** have been determined. The structure of **1** contains a discrete $[ZnL(CH_3COO)]^+$ cation (Fig. 2) and one hexafluorophosphate anion while **2** contains a $[ZnL(H_2O)(ClO_4)]^+$ cation (Fig. 3), one

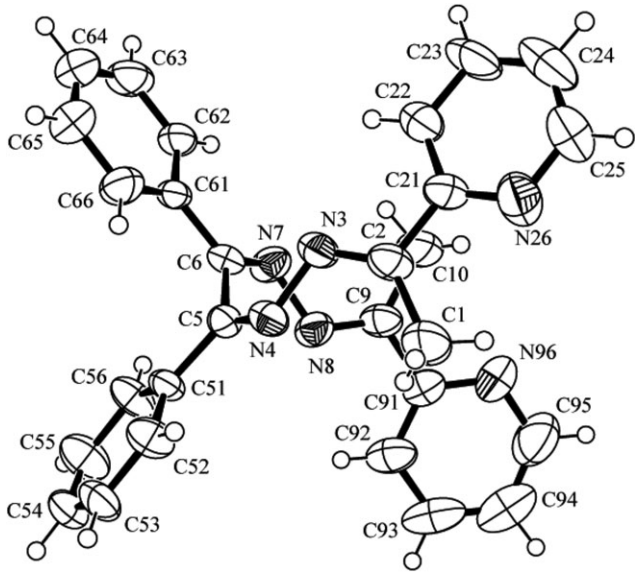


Fig. 1 The structure of L with ellipsoids at 20% probability.

disordered solvent water molecule and one perchlorate anion. The conformations of L in the free state and in the metal complexes are quite similar as shown by the backbone torsion angles in Table 1. The only major difference is in the torsion angle of N(4)–C(5)–C(6)–N(7) which is 88.8(4)° in the free ligand but −64.8(4) and −70.7(7)° in the two

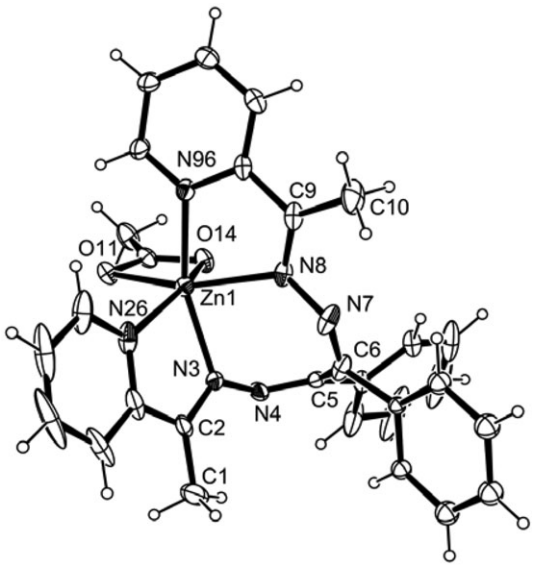


Fig. 2 The structure of the cation $[ZnL(CH_3COO)]^+$ in **1** with ellipsoids at 25% probability. Selected bond lengths (Å) and angles (°): Zn(1)–N(3) 2.092(4), Zn(1)–N(8) 2.218(4), Zn(1)–N(26) 2.110(4), Zn(1)–N(96) 2.080(4), Zn(1)–O(14) 2.128(3), Zn(1)–O(11) 2.176(3); N(3)–Zn(1)–N(8) 82.5(2), N(3)–Zn(1)–N(96) 158.6(2), N(3)–Zn(1)–N(26) 75.7(2), N(3)–Zn(1)–O(14) 96.2(2), N(8)–Zn(1)–N(96) 76.4(2), N(8)–Zn(1)–N(26) 107.1(2), N(8)–Zn(1)–O(14) 98.4(1), N(96)–Zn(1)–N(26) 106.8(2), N(96)–Zn(1)–O(14) 90.6(2), N(26)–Zn(1)–O(14) 151.7(2), N(3)–Zn(1)–O(11) 107.4(2), N(8)–Zn(1)–O(11) 157.4(1), N(26)–Zn(1)–O(11) 95.2(1), N(96)–Zn(1)–O(11) 93.7(1), O(14)–Zn(1)–O(11) 60.9(1).

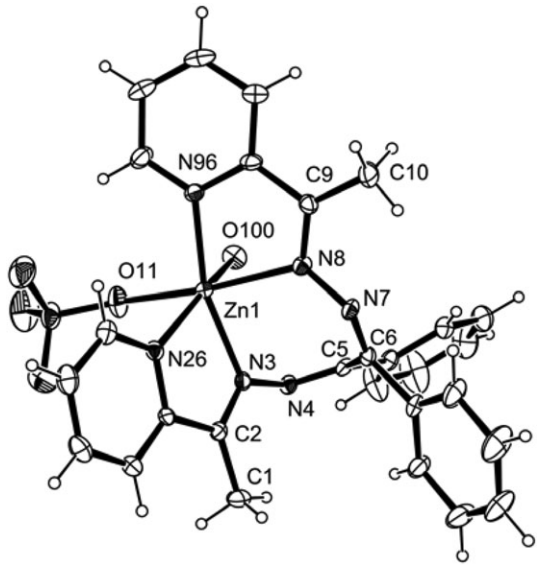


Fig. 3 The structure of the cation $[ZnL(H_2O)(ClO_4)]^+$ in **2** with ellipsoids at 15% probability. Hydrogen atoms on the water molecule were not located. Selected bond lengths (Å) and angles (°): Zn(1)–N(3) 2.087(5), Zn(1)–N(8) 2.187(5), Zn(1)–N(26) 2.129(5), Zn(1)–N(96) 2.051(5), Zn(1)–O(100) 2.171(5), Zn(1)–O(11) 2.257(5); N(3)–Zn(1)–N(8) 84.7(2), N(3)–Zn(1)–N(96) 162.8(2), N(3)–Zn(1)–N(26) 76.1(2), N(3)–Zn(1)–O(100) 92.6(2), N(8)–Zn(1)–N(96) 78.2(2), N(8)–Zn(1)–N(26) 109.1(2), N(8)–Zn(1)–O(100) 87.6(2), N(96)–Zn(1)–N(26) 110.7(2), N(96)–Zn(1)–O(100) 85.4(2), N(26)–Zn(1)–O(100) 158.4(2), N(3)–Zn(1)–O(11) 97.1(2), N(8)–Zn(1)–O(11) 164.2(2), N(26)–Zn(1)–O(11) 86.5(2), N(96)–Zn(1)–O(11) 99.0(2), O(100)–Zn(1)–O(11) 76.6(2).

metal complexes thus facilitating the formation of a seven-membered chelate ring in both the complexes. Metal complexes of L, however, are found to contain such seven-membered chelate rings.[8,9] As such, examples of seven-membered chelate rings are not rare.[10–12] The overall shape of the complexes **1** and **2** is spiral (Fig. 4) as L maintains its helicity in the coordinated mode also. There are many examples of mononuclear single helices in the literature.[9,13–16] Helical complexes are of much current interest because of their morphological similarity with many biologically occurring molecules.

The zinc atom in $[ZnL(CH_3COO)]^+$ is six-coordinate with a distorted octahedral environment. The tetradentate ligand provides four sites of an octahedron around the metal with the remaining two sites occupied by the bidentate acetate anion. The main source of the distortion is the small bite angle, 60.9(1)°, of the acetate ligand. The two Zn–acetate bond lengths are Zn–O(11) 2.128(3) Å and Zn–O(14) 2.176(3) Å. The difference in bond length may be due to the fact that O(11) is *trans* to a pyridine nitrogen N(26), while O(14) is *trans* to an imino nitrogen N(8). Such asymmetrical binding of the acetato group to the metal is observed in many zinc complexes.[5] The two Zn–N(py) distances are 2.080(4) Å for Zn(1)–N(96) and 2.110(4) Å for Zn(1)–N(26). These are comparable to Zn–N(3) at 2.092(4) Å but significantly shorter than Zn–N(8) at 2.218(4) Å.

The coordination sphere of the metal atom in the cation $[ZnL(H_2O)(ClO_4)]^+$ in **2** is also distorted octahedral. The

Table 1 Torsion angles (°) in L and comparison with those in the ligand backbones in the cations in **1** and **2**

Torsion angle	L	$[ZnL(CH_3COO)]^+$	$[ZnL(H_2O)(ClO_4)]^+$
C(1)–C(2)–N(3)–N(4)	1.7(5)	2.2(8)	2.5(8)
C(2)–N(3)–N(4)–C(5)	−136.8(4)	−110.1(6)	−108.4(5)
N(3)–N(4)–C(5)–C(6)	−0.1(4)	12.4(7)	13.8(7)
N(4)–C(5)–C(6)–N(7)	88.8(4)	−64.8(8)	−69.8(7)
C(5)–C(6)–N(7)–N(8)	2.9(4)	2.0(8)	3.6(8)
C(6)–N(7)–N(8)–C(9)	−134.2(3)	−151.7(5)	−144.7(5)
N(7)–N(8)–C(9)–C(10)	4.2(5)	5.7(7)	9.2(8)

binding of the tetradentate ligand is equivalent to that found in **1**, and indeed variations in bond lengths are also similar although in the structure the bidentate acetate anion has been replaced by a mutually *cis* water molecule and perchlorate oxygen atom. The Zn(1)–N(3) bond at 2.087(5) Å is significantly shorter than the Zn(1)–N(8) bond at 2.187(5) Å which is presumably due to the different environments of the two atoms, the former being *trans* to N(96) while the latter is *trans* to the perchlorate oxygen O(11). A similar difference is also observed in **1**.

Complex **2** contains a bound water molecule with a Zn–O distance of 2.171(5) Å. This is on the longer side of the known Zn–O(water) bond lengths in various mono-nuclear Zn complexes containing one coordinated water molecule.[5] Our calculations by the bond valence sum (BVS) model,[17,18] which correlates the bond lengths around a metal center with its oxidation state, shows that the ideal Zn(II)–O bond length in a regular octahedral ZnO_6 core should be 2.11 Å [the required bond valence parameter for the Zn(II)–O bond[17,19] is 1.70 Å]. Incidentally, this length is found in HCA II though the metal ion is in a tetrahedral environment.[2] Anyway, it is apparent from the BVS calculations that the water molecule in **2** is quite strongly bound to the metal.

Complex **2** is not soluble in water. So we decided to measure its pK_a in a non-aqueous solvent like acetonitrile. Since the known methods to determine pK_a in acetonitrile[20–23] do not suit our complex **2** (for example, it does not show any appreciable change in the electronic spectra with deprotonation and consequently spectrophotometric methods are not useful, *etc.*), we wanted to exploit molar conductance to determine the pK_a of **2**. Earlier, Kolthoff and Chantooni have used molar conductance to determine pK_a.[24]

Complex $[ZnL(CH_3COO)]PF_6$ (**1**) is a 1 : 1 electrolyte in acetonitrile. On the other hand, the molar conductance (Λ_{obs}) of $[ZnL(H_2O)(ClO_4)]ClO_4 \cdot H_2O$ (**2**), though expected to be a 1 : 1 electrolyte, in dilute acetonitrile solution exceeds the range specified by Greary[25] for 1 : 2 electrolytes. This means that not only a proton is released in the solution but the ClO_4^- ion also dissociates in acetonitrile. This is a bit surprising as from the Zn(1)–O(11) bond length which is 2.257(5) Å, the perchlorate O seems to be quite strongly bonded to the metal [*cf.* the ideal Zn–O bond length in a symmetric $Zn(II)O_6$ core is 2.11 Å]. Further, the sum of the van der Waals' radii of Zn(II) and O is 3.68 Å.[19] In order to delve into the matter, we have performed some semi-empirical quantum mechanical calculations on the cation $[ZnL(H_2O)(ClO_4)]^+$ in **2** by AM1 method as developed by Dewar.[26] Dewar himself has used AM1 method in the past to model the activity of CA.[27] It is revealed that in the gas phase dissociation of a proton occurs from the cation $[ZnL(H_2O)(ClO_4)]^+$ with concomitant dissociation of the perchlorate ion (Fig. 5). Thus equilibrium (2) is operative for **2**.

$$[ZnL(H_2O)(ClO_4)]^+ \overset{K_a}{\rightleftharpoons} [ZnL(OH)]^+ + H^+ + ClO_4^- \quad (2)$$

The calculated enthalpy change for the equilibrium (2) in the gas phase by AM1 is −227.9 kJ mol^{-1}.

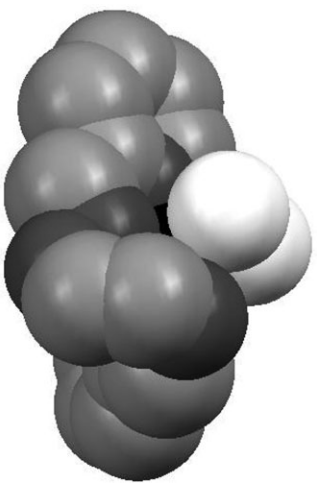


Fig. 4 Helical morphology of the $Zn(L)(O)_2$ moiety in the cations of **1** and **2**. Colour code: N dark grey, C light grey, O white, Zn black.

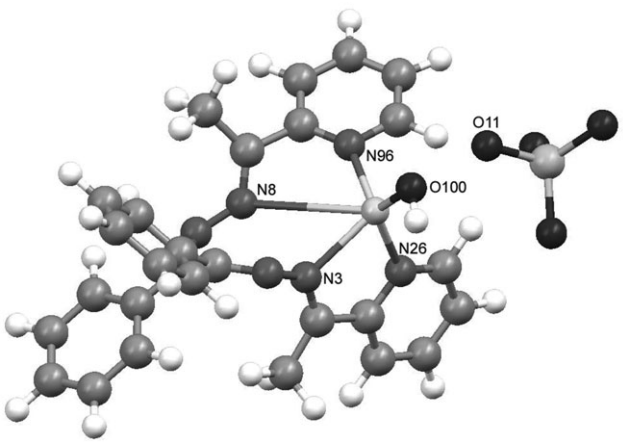


Fig. 5 The gas phase global energy minimum structure of ZnL(OH)-(ClO_4) as obtained by AM1 calculations. Selected bond distances (Å): Zn–O100 1.94, Zn–N26 2.15, Zn–N3 2.32, Zn–N8 3.61, Zn–N96 2.14, Zn–O11 4.32.

Table 2 Conductivity data and determination of pK_a for complex **2** in acetonitrile at room temperature[a]

C	Solution conductance[b]	Λ_{obs}[c]	$[[ZnL(H_2O)]^{2+}]$[d]	$[H^+]$[d]	pK_a[e]
2.068	591	286	0.814	1.254	5.62
1.034	333	322	0.251	0.783	5.72
0.517	180	347	0.070	0.447	5.90
0.259	97	374	0.006	0.252	5.58

[a] C, solute concentration; Λ_{obs}, molar conductance. Various concentrations are given in mmol dm^{-3}. [b] In μohm^{-1}. [c] Molar conductance in ohm^{-1} cm^2 mol^{-1}. [d] Equilibrium concentration. [e] Calculated by eqn (4). Average value is 5.71 (±0.19).

The observed molar conductance (Λ_{obs}) of **2** in acetonitrile is approximately given by eqn (3)

$$\Lambda_{obs} = 140(1 - x) + 380x \quad (3)$$

where x is the molar fraction of dissociated $[ZnL(H_2O)(ClO_4)]^+$, and 140 and 380 ohm^{-1} cm^2 mol^{-1} are, respectively the average values of the molar conductance of a 1 : 1 and a 1 : 3 electrolyte in acetonitrile.[25] For a solute concentration of C mol dm^{-3}, the equilibrium concentration of each of $[ZnL(OH)]^+$, H^+ and ClO_4^- is Cx mol dm^{-3} while that of undissociated $[ZnL(H_2O)(ClO_4)]^+$ is $C(1 - x)$ mol dm^{-3}. Consequently, acid dissociation constant K_a takes the form of eqn (4).

$$K_a = C^2x^3/(1 - x) \quad (4)$$

We have determined the pK_a value by varying the concentration of **2** in the range 10^{-3} to 10^{-4} mol dm^{-3} (Table 2); the average of four determinations is 5.71 (±0.19).

The pK_a value of a compound in water is expected to be lower than that in acetonitrile as water, being more polar than acetonitrile, brings about more ionisation. If ΔG_w^0 is the free energy change for reaction (2) in water and ΔG_s^0 that in acetonitrile, then

$$\Delta pK = pK_s - pK_w = (\Delta G_s^0 - \Delta G_w^0)/2.303RT \quad (5)$$

With $\Delta G^0 = \Delta H^0 - T\Delta S^0$, it follows that

$$\Delta pK = E_s^{sol}([ZnL(OH)]^+) + E_s^{sol}(H^+) + E_s^{sol}(ClO_4^-) - E_w^{sol}([ZnL(OH)]^+) - E_w^{sol}(H^+) - E_w^{sol}(ClO_4^-) + S - E_s^{sol}([ZnL(H_2O)(ClO_4)]^+) + E_w^{sol}([ZnL(H_2O)(ClO_4)]^+) \quad (6)$$

where E^{sol} is the enthalpy of solvation and the term S includes the terms due to differences in entropy changes for reaction (2) in the two solvents water (w) and acetonitrile (s). Recently we have shown that the enthalpy of hydration of the cations can be reproduced very well by an equation like that of Born – eqn (7)

$$E^{sol} = \frac{10^{12}N(Ze)^2}{8\pi\varepsilon_0(r + 53)}\left(\frac{1}{\varepsilon} - 1\right) \quad (7)$$

where N is Avogadro's number, e charge of an electron, ε_0 the permittivity of vacuum, ε the relative permittivity of the medium and r Shannon's crystal ionic radii; the factor of 10^{12} is introduced so that r is expressed in pm.[28] With an experimental value[29,30] of $E_w^{sol}(H^+) = 1100$ kJ mol^{-1} and ε of water[31] as 78.54 and that of acetonitrile[31] as 35.72 at 298 K, $E_s^{sol}(H^+) - E_w^{sol}(H^+)$ is calculated as 16.60 kJ mol^{-1} by using eqn (7). For anions, eqn (7) works quite well with the van der Waals' radii and the correction of 53 pm is not necessary.[28] The ionic volume of ClO_4^- as determined by Mingos and Rohl[32] is 47×10^6 pm^3 which yields a radius of 225 pm. Accordingly, $E_s^{sol}(ClO_4^-) - E_w^{sol}(ClO_4^-)$ comes out as 4.72 kJ mol^{-1}. From X-ray crystal structures, the radii of the cations $[ZnL(H_2O)(ClO_4)]^+$ and $[ZnL(OH)]^+$ are roughly estimated as 600 pm. Adding 53 pm to it, use of eqn (7) yields $E_s^{sol}([ZnL(OH)]^+) - E_w^{sol}([ZnL(OH)]^+) - E_s^{sol}([ZnL(H_2O)(ClO_4)]^+) + E_w^{sol}([ZnL(H_2O)(ClO_4^-)]^+) \approx 0$ kJ mol^{-1}. Hence, from eqn (6), it follows

$$\Delta pK = 21.32 \text{ kJ mol}^{-1} + S \quad (8)$$

As such, the terms in S are small ($T\Delta S$ for proton in water[30] is only 12.1 kJ mol^{-1}) and their differences in the two solvents are also expected to be small enough. Thus with $S \rightarrow 0$, ΔpK is expected to be 3.71 pK unit.

The above exercise of ours shows that had **2** been soluble in water, its pK_a value in water would be less than that in acetonitrile by at least 3.71 pK_a unit [equivalent to 21.32 kJ mol^{-1}; see eqn (8)]. Accordingly, our complex **2** is most acidic among all the known mononuclear monoaqua complexes of zinc.[5] However, all our attempts to isolate the corresponding OH complex has so far failed. For example, reaction of triethylamine with **2** in acetonitrile leaves the compound unchanged. Complex **2** dissolves in 1 : 1 mixture of dioxane–water. Addition of stoichiometric amount of KOH to such a solution to generate the corresponding hydroxo compound leads to the isolation of the free ligand in almost quantitative yield. Many monohydroxo compounds of zinc are known to be unstable.[5] Our AM1 calculations show that enthalpy change for reaction (9) in the gas phase is −262.1 kJ mol^{-1} which possibly explains why we obtain the free ligand in the presence of OH^-.

$$[ZnL(H_2O)(ClO_4)]^+ + OH^- + 4H_2O \rightarrow L + ClO_4^- + [Zn(H_2O)_5(OH)]^+ \quad (9)$$

Complex **2** does not evolve CO_2 in its reaction with bicarbonate in acetonitrile. Heterogeneous reaction of **2** with $NaHCO_3$ in acetonitrile leads to the dissolution of the bicarbonate with stirring, but finally from the solution only free ligand can be isolated. Again, **2** does not react with CO_2 in acetonitrile in presence of a base like triethylamine. Thus complex **2** is not at all effective in bringing about the hydration of CO_2 [reaction (1)]. Further, addition of acetate ion in a solution of **2** does not yield **1**.

Concluding remarks

Here we have synthesised and characterised two complexes of zinc with a tetradentate N-donor helical ligand L. When the anion is acetate, we obtain an acetato coordinated octahedral Zn complex (**1**) and with perchlorate, we obtain a monoaqua zinc complex (**2**) where a perchlorate anion binds the metal. Thus both the complexes contain a ZnN_4O_2 core. However, they are not interconvertible. Complex **2** is highly acidic. Had it been soluble in water, its pK_a value in water would have been ~2. Its proton dissociation is accompanied with simultaneous

release of the coordinated perchlorate anion from the metal coordination sphere. That is upon deprotonation, there occurs a contraction in the coordination sphere of zinc in **2**. Such a phenomenon is unprecedented in the chemistry of zinc aqua complexes. However, recently, we have shown by means of PM3 calculations that certain metal aqua ions like $[Tl(H_2O)_6]^{3+}$ undergoes contraction in the metal coordination sphere upon deprotonation by losing bound water molecules.[28] Release of a proton and a perchlorate anion from the cation $[ZnL(H_2O)(ClO_4)]^+$ in **2** generates $[ZnL(OH)]^+$ [reaction (2)]. The monohydroxo species $[ZnL(OH)]^+$ could not be isolated in the solid state. Our AM1 calculations show that Zn in $[ZnL(OH)]^+$ is distorted tetrahedral as one of the four binding N atoms forms a very long bond with the metal (Zn–N8 3.61 Å; Fig. 5). The zinc center in CA is actually distorted tetrahedral with a N_3O core. Still our complex **2** does not result in the hydration of CO_2 which is the main function of the carbonic anhydrases.

Experimental

General

$Zn(ClO_4)_2 \cdot 6H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$ and NH_4PF_6 were purchased from Aldrich. Ligand L was synthesised by a procedure reported earlier by us.[6] Purified acetonitrile was used for conductivity measurements which were made by a Systronics (India) conductivity meter (Model 304). Microanalyses were performed by a Perkin-Elmer 2400II elemental analyser. UV/Vis spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer, FTIR spectra on a Shimadzu FTIR-8400S spectrometer, 300 MHz NMR spectra (reference: TMS) on a Bruker DPX300 spectrometer. AM1 calculations were performed by using HyperChem (version 6.0).

Syntheses

CAUTION! Though while working with **2** we have not met with any incident, care should be taken in handling it as perchlorates are potentially explosive. It should not be prepared and stored in large amounts.

$[ZnL(CH_3COO)]PF_6$ (1). 0.110 g (0.5 mmol) of $Zn(CH_3COO)_2 \cdot 2H_2O$ dissolved in 5 ml of methanol was added dropwise to a 20 ml solution of 0.224 g (0.5 mmol) of L and stirred for 30 min. To the resulting yellow solution, 0.085 g (0.5 mmol) of NH_4PF_6 dissolved in 5 ml of methanol was added and stirred for another 30 min. The precipitated yellow compound was filtered off, washed with a few drops of petroleum ether and dried in air. Yield, 0.180 g (50%). Yellow single crystals were obtained by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex. Anal. Found (calc.): C, 50.29 (50.43); H, 3.97 (3.81); N, 11.65 (11.77)%. FTIR ν/cm^{-1} (KBr): 839vs (PF_6). UV/Vis (CH_3CN) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 253 (21 200), 311 (25 800). ^1H NMR (CD_2Cl_2): δ 1.84 (3H, s, methyl protons of acetate), 2.70 (6 H, s, methyl protons of L), 7.44–8.84 (18 H, aromatic protons). ^{13}C NMR (CD_2Cl_2): 15.88 (methyl C of L), 21.48 (methyl C of acetate), 125.40–165.27 (aromatic and tertiary C's), 181.60 (carboxylate C).

$[ZnL(H_2O)ClO_4]ClO_4 \cdot H_2O$ (2). 0.186 g (0.5 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ dissolved in 3 ml of tetrahydrofuran was added dropwise to a 10 ml tetrahydrofuran solution of 0.224 g (0.5 mmol) of L with stirring. Within 2 min of stirring, a yellow compound started appearing. After stirring for 30 min, the precipitated yellow compound was filtered off, washed with a few drops of petroleum ether and dried in air. Yield, 0.3 g (83%). Yellow single crystals were obtained by direct diffusion of diethyl ether into a dilute acetonitrile solution of the complex. Anal. Found (calc.): C, 45.29 (45.13); H, 3.69 (3.79); N, 11.20 (11.28)%. FTIR ν/cm^{-1} (KBr): 1090vs, 625s (ClO_4). UV/Vis (CH_3CN) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 202 (54 700), 244 (27 100), 312 (32 100). ^1H NMR (DMSO-d_6): δ 2.26 (6 H, s, methyl protons), 7.36–8.57 (18 H, aromatic protons). ^{13}C NMR (DMSO-d_6): 14.16 (methyl C), 120.89–162.81 (aromatic and tertiary C's).

X-Ray crystallography

Data for L and **2** were measured with Mo-Kα radiation using the MARresearch Image Plate System at 293 K. The crystals were positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[33] Data for **1** were measured with Mo-Kα radiation using the Oxford Diffraction X-Calibur CCD system at 150 K. The crystal was positioned at 50 mm from the CCD and 321 frames were measured with a counting time of 2 s. Data analysis was carried out with the Crysalis program[34] to provide 8780 independent reflections. The structures were solved using direct methods with the SHELXS97 program.[35] In **1**, one of the phenyl rings occupied two different orientations each with 50% occupancy. There is a solvent water molecule in **2** disordered over three sites, all given 1/3 occupancy. Apart from these disordered atoms, in all three structures, the non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms on O100 in **2** could not be located. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Empirical absorption corrections were carried out on **1** using DIFABS[36] and **2** using ABSPACK.[37] The structures were refined on F^2 using SHELXL97.[35]

L. $C_{28}H_{24}N_6$, M_w = 444.53, triclinic, space group $P\bar{1}$, a = 9.884(14), b = 11.444(14), c = 12.684(17) Å, α = 74.40(1), β = 77.90(1), γ = 66.15(1)°, U = 1256(3) Å^3, Z = 2, D_c = 1.176 g cm^{-3}, μ = 0.072 mm^{-1}, 6781 reflections collected, 4092 independent, R_{int} = 0.0924, $R1$ = 0.0695 and $wR2$ = 0.1646 for 1813 reflections with $I > 2\sigma(I)$.

$[ZnL(CH_3COO)]PF_6$ (1). $C_{30}H_{27}F_6N_6O_2PZn$, M_w = 713.92, monoclinic, space group $P2_1/c$, a = 12.7999(11), b = 14.3093(15), c = 17.1281(13) Å, β = 103.118(7)°, U = 3055.3(5) Å^3, Z = 4, D_c = 1.553 g cm^{-3}, μ = 0.933 mm^{-1}, 19 349 reflections collected, 8780 independent, R_{int} = 0.0746, $R1$ = 0.0776 and $wR2$ = 0.1984 for 3195 reflections with $I > 2\sigma(I)$.

$[ZnL(H_2O)(ClO_4)]ClO_4 \cdot H_2O$ (2). $C_{28}H_{28}Cl_2N_6O_{10}Zn$, M_w = 748.83, monoclinic, space group $P2_1/n$, a =

10.263(11), b = 15.745(17), c = 21.37(2) Å, β = 103.11(1)°, U = 3364(6) Å^3, Z = 4, D_c = 1.487 g cm^{-3}, μ = 0.951 mm^{-1}, 21 180 reflections collected, 6402 independent, R_{int} = 0.0588, $R1$ = 0.0875 and $wR2$ = 0.1637 for 5237 reflections with $I > 2\sigma(I)$.

CCDC reference numbers 637424, 649827 and 649828.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706230n

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