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X-ray Crystal Structure and Characterization in Aqueous Solution of {*N*,*N*′-Ethylenebis(pyridoxylaminato)}zinc(II)

Isabel Correia,[a] Agnes Dornyei,[b] Fernando Avecilla,[c] Tamás Kiss,*[b] and João Costa Pessoa*[a]

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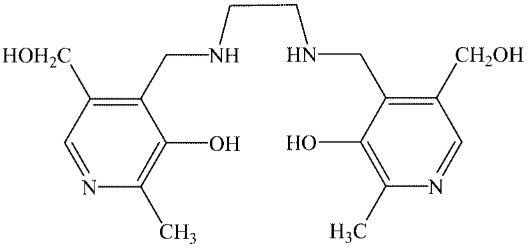
The complexation of Zn^{II} with H_2Rpyr_2en [H_2Rpyr_2en = *N*,*N*′-ethylenebis(pyridoxylaminato)] in aqueous solution has been studied by pH potentiometry and ^1H NMR spectroscopy. Complex formation constants are determined and binding modes proposed. Complex formation starts at around pH 4, and several species with a 1:1 ligand-to-metal ratio with different protonation states form up to pH 12. Only above pH 10 does a hydrolytic species $[ZnLH_{-1}]^-$ become important. The crystal and molecular structures of $[ZnCl(H_2Rpyr_2en)]^+Cl^- \cdot 1.5H_2O$ (**1**) have been determined by X-ray diffraction. The coordination of the H_2Rpyr_2en ligand involves the two phenolate-O and two amine-N atoms in a distorted square-pyramidal geometry. The two pyridine-N atoms are protonated, and a Cl^- atom completes the coordination sphere. Upon coordination, both N-amine atoms of H_2Rpyr_2en become stereogenic centres, and in both molecules of the unit cell of **1** one of the N-amine donors has an (*R*)-configuration, and the other an (*S*)-configuration.

Introduction

Sal_2en-type ligands are known to coordinate several metal ions in different oxidation states and are among the most studied/important ligand systems used in asymmetric catalysis.[1–3] Their reduced derivatives (frequently named tetrahydrosalen or salan ligands),[4] are much less studied and exhibit different structural and chemical properties: the presence of an amine backbone (instead of an imine) results in a more flexible structure that is also more resistant to hydrolysis of the C–N bond. Moreover, the N-amine atoms become stereogenic centres upon coordination, and this may lead to complexes that give a higher enantiomeric excess when used in catalysis.

Despite the interest of zinc sal_2en complexes as models of the active site of carbonic anhydrase and other zinc-containing enzymes,[4–6] they are not easily obtained. Their low solubility in most common solvents is another drawback, and only a few complexes have been characterized by X-ray diffraction. The Zn^{II} ion in these complexes is either five-coordinate with a square-pyramidal geometry[6,7] or has a dinuclear structure.[8] Singer et al.[6] have characterized two mononuclear zinc complexes with sal_2en-type SB's (SB = Schiff base) containing a solvent molecule in a fifth coordination position. When using a reduced derivative they obtained a dinuclear arrangement with a trigonal-bipyramidal geometry around the metal ion.

We recently[9] reported the synthesis and characterization of the SB *N*,*N*′-ethylenebis(pyridoxylideneiminato) (pyr_2en) and of its reduced derivative *N*,*N*′-ethylenebis(pyridoxylaminato) (H_2Rpyr_2en; structure depicted in Scheme 1). Both compounds are vitamin B_6 analogues and are water-soluble, and several vanadium-based $Rpyr_2en$ complexes have been prepared and characterized.[9,10] Two molecular structures were obtained for the dioxovanadium(V) complexes[9,10] with H_2Rpyr_2en, which emphasises the flexibility of the ligand when coordinated to the metal ion.



Scheme 1. Formula of H_2Rpyr_2en (H_2L), which is a water-soluble compound. It may be considered as two pyridoxamine molecules linked by an ethylene bridge. In its fully protonated form the molecule corresponds to H_6L^{4+}, and in its totally deprotonated form to L^{2-}. As a ligand it may coordinate through the two amine-N and two phenolate-O atoms, either with both pyridine-N atoms protonated (H_2L), monoprotonated (HL^-), or deprotonated (L^{2-}).

Several vanadium complexes have been shown to be insulin mimetics,[11–13] namely vanadium–$Rpyr_2en$ com-

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[a] Centro Química Estrutural, Instituto Superior Técnico,
Av. Rovisco Pais, 1049-001, Lisbon, Portugal
[b] Department of Inorganic and Analytical Chemistry, Biocoordination Chemistry Research Group of the Hungarian Academy of Sciences, University of Szeged,
PO Box 440, 6701 Szeged, Hungary
[c] Departamento de Química Fundamental, Universidade da Coruña, Campus de A Zapateira,
15071 A Coruña, Spain

plexes.[9,10,14,15] Zinc–$Rpyr_2en$ complexes may also be good candidates as insulin mimetics,[16] and in this work we report the preparation of Zn^{II}–H_2Rpyr_2en complexes and the characterisation of $[ZnCl(H_2Rpyr_2en)]^+Cl^- \cdot 1.5H_2O$ (**1**) by X-ray diffraction. The molecular structure of **1** shows that the H_2Rpyr_2en ligand is tetracoordinated in a distorted square-pyramidal geometry, with a chlorine atom completing the coordination sphere. The aqueous solution behaviour of the Zn^{II} + H_2Rpyr_2en system has been studied by pH-potentiometry and ^1H NMR spectroscopy.

Results and Discussion

Synthesis and Characterization

A white solid, which was characterized by elemental analysis and ^1H NMR and IR spectroscopy, was obtained from an aqueous solution containing H_2Rpyr_2en and $ZnCl_2$ (1:1) at pH 9.5. The elemental analysis results are consistent with the formulation $Zn(Rpyr_2en) \cdot 5H_2O$. All ^1H NMR peaks of the compound dissolved in D_2O at pH 7.6 are broad, and only the peaks assigned to CH_2N clearly show two resonances (see Exp. Sect.).

Colourless crystals of $[ZnCl(H_2Rpyr_2en)]^+Cl^- \cdot 1.5H_2O$ (**1**) were obtained from an alcoholic solution containing zinc acetate, H_2Rpyr_2en and Cl^- (from HCl, which was used to set the pH) and characterized by single-crystal X-ray diffraction. Figure 1 shows an ORTEP diagram with the atom labelling scheme, and Table 1 contains selected bond lengths and angles. The molecule is cationic, with both pyridine N-atoms protonated, and the H_2Rpyr_2en ligand is tetracoordinated through the two $O_{phenolate}$ and the two N_{amine} atoms. A chloride in the axial position completes the coordination sphere of the metal. The molecule is not planar, but presents a shape similar to an open umbrella. The geometry that best describes the metal centre is square-pyramidal, with the H_2Rpyr_2en donor atoms occupying the basal plane and the Cl^- the apical position. The flexibility of the ligand can be analysed in terms of the deformation of the N_2O_2 plane and the displacement of the zinc ion from it. The rms deviation of the four donor atoms O(1)–N(1)–N(2)–O(2) from planarity is 0.0140(16) Å; the central Zn(1) ion lies 0.5105(17) Å above the plane. These values indicate that there is a significant deformation of the coordination plane, which is greater than in other Zn–sal_2en complexes.[5,17] The Zn–$O_{phenolate}$ bond lengths are within the normal range for this type of bonds,[6,18,19] as are the Zn–N_{amine} and Zn–Cl bonds.[6,20,21] Overall, the complex has one positive charge and the counterion is a chloride, which is 7.76 Å away from the zinc centre. The C–O bond lengths are normal for phenolate-O atoms coordinated to zinc (1.318 and 1.296 Å),[18,19] and the C–N distances (1.480–1.483 Å) are typical of single bonds.[6,20] There are no important changes in the C–N_{amine} bond lengths upon coordination to the zinc ion – they increase by less than 0.012 Å – but the C–$O_{phenolate}$ bonds decrease by more than 0.03 Å (0.061 Å for one of them).[9]

Both pyridoxal rings are approximately planar, with rms deviations from the plane of the six atoms of 0.0183(27) and 0.0114(28) Å. The ligand is quite flexible, this being evidenced, for example, by the torsion angles between N(1)–C(2)–C(1)–N(2), C(4)–C(3)–N(1)–C(2) and C(11)–C(10)–N(2)–C(1), which are 57.7(5)°, 168.9(3)° and 176.3(5)°, respectively. Some relevant H-bonds in the crystal packing (see Figure 2) are included in Table 1.

Comparing this structure with that reported for $[Zn^{II}(pyridoxamine)_2(H_2O)_2](NO_3)_2$,[22] several differences become clear, namely i) that the pyridoxamine complex corresponds to an octahedral geometry, and ii) the Zn–N_{amine} bond lengths are shorter than the Zn–O bonds, which is probably due to the different coordination number and to the higher steric requirement in the Zn–H_2Rpyr_2en complex.

The IR spectra of the Zn–H_2Rpyr_2en complexes in the powder and crystalline forms are similar. They are quite complex in the 2600–3500 cm^{-1} range, which contains several bands assigned to stretching (symmetrical and asym-

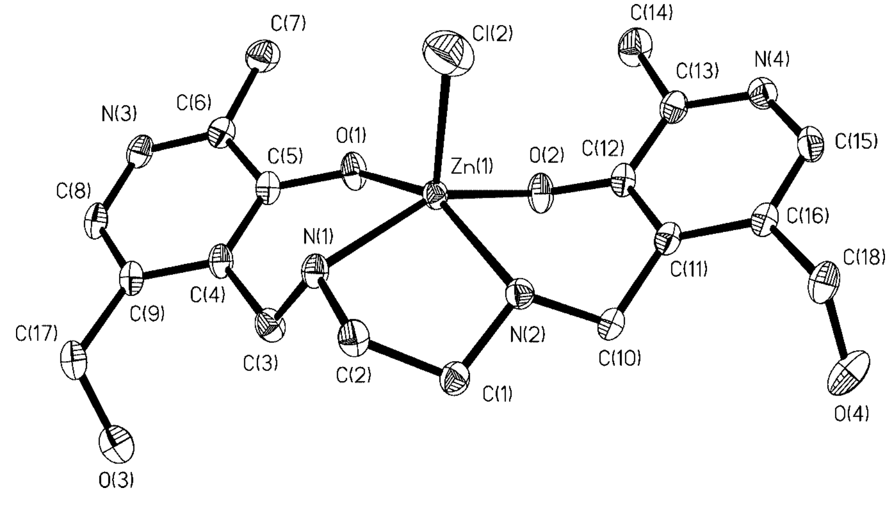


Figure 1. ORTEP diagram of $[ZnCl(H_2Rpyr_2en)]^+Cl^- \cdot 1.5H_2O$ (**1**) showing the atom labelling scheme. The ligand coordinates through the two amine-N and two phenolate-O atoms, with both pyridine-N atoms protonated. The thermal ellipsoids are drawn at 30% probability level. The hydrogen atoms and water molecules are not included, namely those bound to the pyridine N atoms N(3) and N(4).

Table 1. Selected bond lengths [Å], angles [°] and hydrogen-bonds parameters for $[ZnCl(H_2Rpyr_2en)]^+Cl^-\cdot 1.5H_2O$ (**1**).

Bond lengths [Å]		Angles [°]		A···H–D	A–D [Å]	A···H–D [°]	Symmetry code
Zn(1)–O(1)	1.976(3)	O(1)–Zn(1)–O(2)	88.96(11)	Cl(1)···H–N(4)	3.078(4)	164(5)	
Zn(1)–O(2)	2.026(3)	O(1)–Zn(1)–N(1)	88.00(11)	Cl(1)···H–O(4)	3.120(4)	161(6)	$x + 1, y, z$
Zn(1)–N(1)	2.167(3)	O(2)–Zn(1)–N(1)	150.66(13)	O(3)–H···O(1)	2.735(4)	149(5)	$-x, -y + 2, -z + 2$
Zn(1)–N(2)	2.159(4)	O(1)–Zn(1)–N(2)	151.80(13)	O(3)–H···O(2)	3.203(4)	124(5)	$-x, -y + 2, -z + 2$
Zn(1)–Cl(2)	2.2282(18)	O(2)–Zn(1)–N(2)	88.16(12)	O(3)–H···O(1W)	2.794(5)	166(7)	$x - 1, y, z$
O(1)–C(5)	1.318(4)	N(1)–Zn(1)–N(2)	81.00(12)	O(1W)–H···N(3)	2.760(5)	165.9(8)	
O2–C(12)	1.296(5)	O(1)–Zn(1)–Cl(2)	106.38(10)				
N(2)–C(1)	1.464(5)	O(2)–Zn(1)–Cl(2)	104.37(10)				
N(2)–C(10)	1.480(5)	N(1)–Zn(1)–Cl(2)	104.48(10)				
N(1)–C(2)	1.478(5)	N(2)–Zn(1)–Cl(2)	101.51(10)				
N(1)–C(3)	1.483(5)						

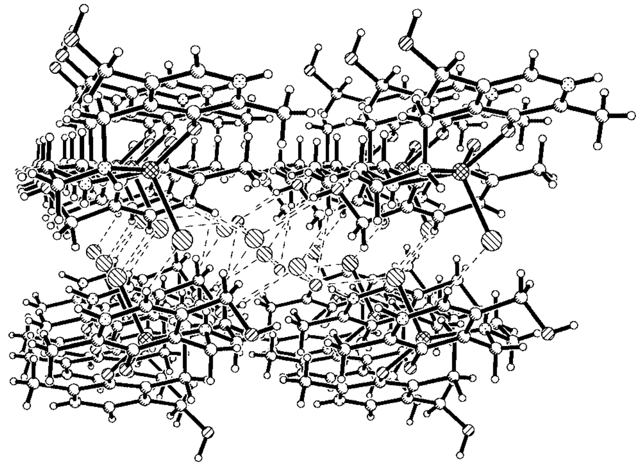
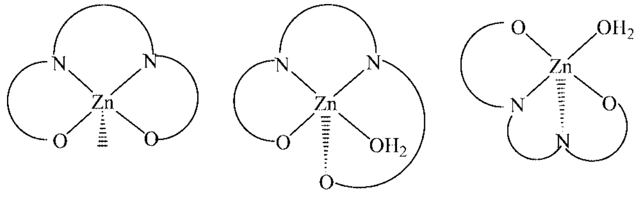


Figure 2. Crystal packing of the $[ZnCl(H_2Rpyr_2en)]^+Cl^-\cdot 1.5H_2O$ molecules, showing the hydrogen-bonding network.

metrical) of the hydrogen-bonded CH_2O–H groups of the pyridoxal ring and water molecules.[23,24] The ν(N–H) absorption, which is present in the ligand spectrum at 3286 cm^{-1},[9] appears at 3210 and 3261 cm^{-1} in the crystal and powder complexes, respectively, in agreement with the coordination through the amine-N atoms. The $\nu(C–O)_{phenolate}$ absorptions are in the expected range for this type of compounds at 1294 and 1296 cm^{-1}, respectively.[23,24] The two $\nu(N_{pyridine}$–H) absorptions appear at 3317 and 3340 cm^{-1} in the spectrum of the crystal.

We found[9] that two main types of isomers, which correspond to different energies, form in solution for the $V^{IV}O$– and V^VO_2–H_2Rpyr_2en complexes. For the $V^{IV}O$ complexes, two types of binding modes can form, one with the two N-amines and two O-phenolates as equatorial donors, and the other with one of these donor atoms in an axial position, the fourth equatorial donor atom now being an O atom from a water ligand. The two types of isomers give distinct peaks in the EPR spectrum (for the $V^{IV}O$ complexes), and for the V^VO_2 complexes two broad ^{51}V NMR resonances and two distinct ^1H NMR peaks are observed for all H-atoms. If similar isomers were to form in solution for the Zn^{II}–H_2Rpyr_2en system (see Scheme 2, type I and type II isomers), we would also expect the observation of distinct ^1H NMR resonances for the H-atoms of the isomers with either one O-phenolate (type IIA) or one N-amine (type IIB) in an axial position. However, this is not the case (see below), therefore only one type of isomer forms, namely the one with a binding mode similar to that found for **1**, but with no apical Cl^- donor atom, i.e. type I in Scheme 2. For similar complexes with $[V^{IV}O\{R(SO_3\text{-sal})_2en\}]$ (SO_3-sal = salicylaldehyde-5-sulfonate), we have also observed that the isomers with one equatorial H_2O ligand essentially do not form.[10]



Type I **Type IIA** **Type IIB**

Scheme 2. Schematic representation of the main types of isomeric complexes that may form in solution.

As the coordinated N-amine atoms of H_2Rpyr_2en are stereogenic centres, two main types of stereoisomeric complexes may form for the type I binding mode, namely those with both N-amine donors either *R* or *S*, and those with one *S* and one *R*. As found for the $V^{IV}O$– and V^VO_2–H_2Rpyr_2en complexes,[9] we could expect that for the Zn^{II}–H_2Rpyr_2en system these isomeric complexes also correspond to approximately similar energy. In the ^1H NMR spectra of **1** the peaks are relatively broad, and only in the case of the CH_2NH resonances are separate peaks observed.

Speciation Studies

pH-Potentiometry

The acid–base behaviour of H_2Rpyr_2en and its complex formation with $V^{IV}O$ and V^V have been reported previously.[9] The study of the Zn^{II}–H_2Rpyr_2en system by pH-potentiometry and ^1H NMR spectroscopy is presented here. The pH-metric titration curves were measured between pH 2.2 and 11.7, and the evaluation was made by considering a model similar to that obtained for the $V^{IV}O$ system, which corresponds to the best model fitting the experimental data. The formation constants are listed in

Table 2 and a species-distribution diagram is depicted in Figure 3.

Table 2. Protonation (p*K*) and Zn^{II} complex ($M_pL_qH_r$) formation constants (log *β*) with H_2Rpyr_2en at I = 0.2 M (KCl) and 25 °C.[a]

	log *β*	p*K*
H_6L^{4+}	38.46	2.20
H_5L^{3+}	36.26	3.01
H_4L^{2+}	33.25	5.96
H_3L^{+}	27.29	7.66
H_2L	19.63	9.13
HL^{-}	10.50	10.50
$[ZnLH_2]^{2+}$	27.08 (1)	7.44
$[ZnLH]^{+}$	19.64 (2)	8.11
ZnL	11.53 (2)	10.80
$[ZnLH_{-1}]^{-}$	0.72 (2)	
No. of points	481	
Fitting[b] [mL]	5.61×10^{-3}	

[a] Three times the standard deviation is reported in parentheses. [b] The average difference between the calculated and the experimental titration curves, expressed in millilitres of titrant. The total initial volumes were 25 mL.

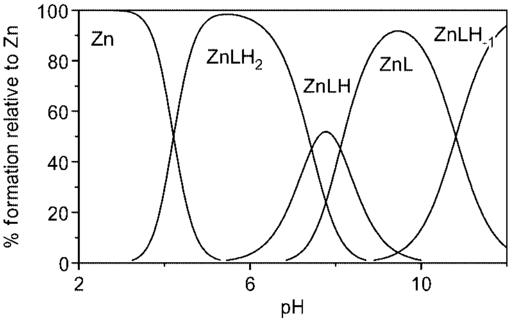


Figure 3. Species-distribution diagram for the complexes formed in the Zn^{II}–H_2Rpyr_2en system; C_{Zn} = 2.0 mM and L/M = 2.

Analysis of the potentiometric data with the PSEQUAD program[25] showed the presence of only 1:1 complexes of different protonation states ($[ZnLH_2]^{2+}$, $[ZnLH]^+$, [ZnL] and $[ZnLH_{-1}]^-$) in the pH range studied. Coordination starts at around pH 4 with the displacement of four protons from the ligand to form $[ZnLH_2]^{2+}$. Further deprotonation, now involving the pyridine-N atoms, results in the progressive formation of $[ZnLH]^+$ and [ZnL]. Above pH 10 a hydrolytic species, $[ZnLH_{-1}]^-$, becomes important. Upon comparison with the $V^{IV}O$–, Ni^{II}– and Cu^{II}–H_2Rpyr_2en systems,[9,26] the proton displacement constants (*K**), which refer to the process $H_6L + M^{2+} \rightleftharpoons MLH_2^{2+} + 4H^+$ [$K^*(CuLH_2^{2+}) = -3.24$; $K^*(V^{IV}OLH_2^{2+}) = -5.63$; $K^*(NiLH_2^{2+}) = -10.08$; $K^*(ZnLH_2^{2+}) = -11.38$], give the stability order $Cu^{II} > V^{IV}O > Ni^{II} > Zn^{II}$.

Complexation of Zn^{II} with a hexadentate diacetic acid derivative of H_2Rpyr_2en, namely PLED (*N*,*N*′-dipyridoxyethylenediamine-*N*,*N*′-diacetic acid),[27–29] presents a similar speciation, although with a higher stability for the complex formed {$K^*(ZnLH_2) = -5.33$ [T = 25 °C, I = 0.1 M (NaCl)]} due to the hexadentate coordination of the ligand.[29]

¹H NMR Spectroscopic Studies

The acid–base properties and the protonation scheme of $Rpyr_2en^{2-}$ have been studied by ¹H NMR spectroscopy and pH-potentiometry previously.[9] The formation of H bonds between the phenolic and the amino groups is favourable as the phenolic protons are quite acidic and are even more acidic than those of pyridoxamine.[9] Figure 4 shows the ligand, the atom labelling scheme used in the ¹H NMR spectra and the pH-dependence of the chemical shifts for solutions containing a total Zn^{II} concentration (C_{Zn}) of 4 mM and a ligand-to-metal (L/M) ratio of 2.

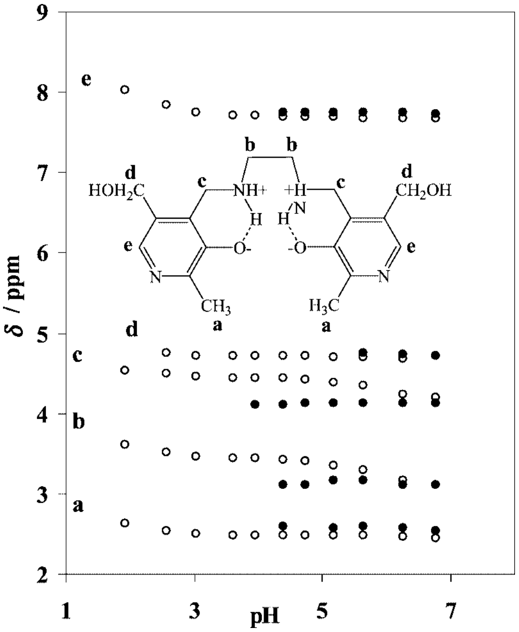


Figure 4. pH-dependence of the chemical shifts (*δ* in ppm) of the ligand protons in the absence (open circles) and the presence of Zn^{II} ion (L/M = 2, full circles); C_{ligand} = 8 mM. The H_2Rpyr_2en molecule and the proton-labelling scheme are also depicted in the figure.

The complex formation of H_2Rpyr_2en with Zn^{II} was also studied by ¹H NMR spectroscopy by measuring spectra at room temperature for L/M ratios of 1 and 2, with C_{Zn} = 4 mM. Below pH 4 no complexes could be detected in solution, all peaks being directly assignable to the free ligand. At a pH of around 4, however, where complex formation starts (see Figure 3), the peaks broaden, then new, slightly shifted peaks appear for all protons (see Figure 5), i.e. separate peaks can be ascribed to protons in the free and the complexed ligand, suggesting an exchange that is somewhat slower than the NMR timescale. The peaks of protons **a**, **e** and **d** in the complexes are slightly deshielded relative to the ligand, while protons **b** and **c** are shielded. Precipitation occurs above pH 7. This is probably due to the higher concentrations used in the ¹H NMR titrations. Moreover, while in the pH-metric titrations the equilibrium was reached very rapidly, in the ¹H NMR titrations a few minutes were required to stabilize the pH readings.

Due to the presence of the amine bonds (instead of imine as in sal_2en-type ligands) H_2Rpyr_2en is a more flexible molecule and its coordination does not yield similarly symmetrical complexes. As mentioned above, the coordinated amine-N atoms of H_2Rpyr_2en are stereogenic centres, and for binding mode I (Scheme 2) several stereoisomers may

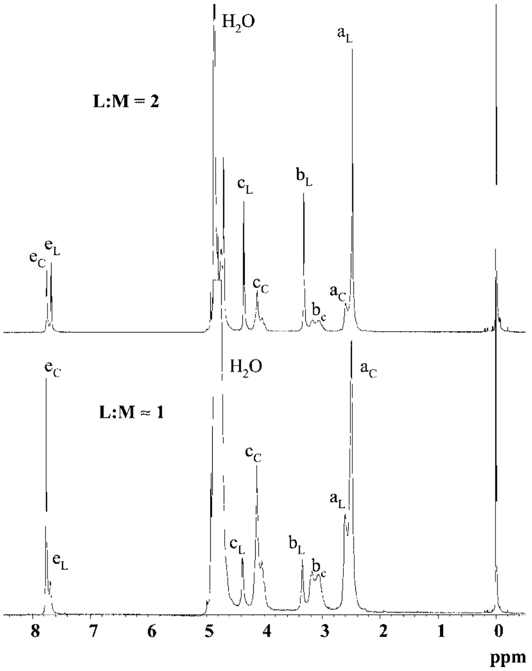


Figure 5. ^{1}H NMR spectra for solutions containing Zn^{II} (C_{Zn} = 4 mM) and H_2Rpyr_2en at pH 5.47. The approximate L/M ratios and the peak assignments are indicated. See Figure 4 for the proton-labelling scheme. The subscripts L and C mean free and coordinated ligand, respectively. For the spectrum shown at L/M ≈ 1, a small excess of ligand is present.

form as both amine donors may be either *R* or *S*, or both *S*, or both *R* (three isomers for $ZnLH_2$ and ZnL stoichiometries and four for the ZnLH stoichiometry).

This is probably the reason why two peaks are observed for the protons of the CH_2CH_2 and CH_2N groups in the coordinated ligand. The intensity ratios of these peaks are not clear as some are broader than others, and they strongly overlap, but from the NMR spectra the intramolecular nonequivalence of these protons is clear.

Overall, and despite some different experimental conditions (e.g. ionic strength, equilibrium time and concentrations), the spectroscopic results confirm the pH-metric data obtained for the Zn^{II}–H_2Rpyr_2en system.

Conclusions

The coordination of Zn^{II} to H_2Rpyr_2en has been investigated. The complexes have moderate solubility in aqueous solution. The compound $[ZnCl(H_2Rpyr_2en)]^+Cl^-\cdot 1.5H_2O$ (**1**) has been characterized by single-crystal X-ray diffraction, thereby confirming the flexibility of the reduced Schiff base as compared with the Schiff base pyr$_2$en. In the molecular structure of **1**, one of the coordinated amine-N atoms has an (*S*)-configuration and the other an (*R*)-configuration. All combinations of these configurations presumably occur in solution, and in the ^{1}H NMR spectra either broader peaks and/or two distinct resonances are observed for the hydrogen atoms of the coordinated ligand, namely for the H atoms of the $CH_2NCH_2CH_2NCH_2$ moiety. The H_2Rpyr_2en ligand in **1** is coordinated through the two phenolate-O and amine-N atoms in a distorted square-pyramidal geometry. To the best of our knowledge this is the first example of a monomeric Zn^{II}–reduced salen-type SB that does not dimerize. The solution studies have revealed the high stability of the Zn^{II} complexes formed, although they are less stable than those formed by H_2Rpyr_2en with Cu^{II}, Ni^{II} or V^{IV}O. Vanadium and copper complexes with chiral sal$_2$an type ligands are presently being tested for catalytic asymmetric synthesis. The additional stereogenic centres formed upon coordination of the N-amine donors may favour higher enantiomeric excesses in some of these catalytic systems.

Experimental Section

H_2Rpyr_2en: The synthesis of this ligand has been reported previously.[9]

$[Zn(Rpyr_2en)]\cdot 5H_2O$: H_2Rpyr_2en (66mg, 0.18 mmol) was dissolved in 10 mL of H_2O containing a few drops of 1 M HCl. $ZnCl_2$ (10.2 mL of a 0.0156 M solution) was added and the pH adjusted to 9.5 with 1 M KOH. The solution was stirred for one hour, and a white precipitate was removed by filtration, washed with ethanol and diethyl ether and dried under vacuum. $C_{18}H_{24}N_4O_4Zn\cdot 5H_2O$ (515.9): calcd. C 41.91, H, 6.64, N 10.86; found C 42.2, H 7.0, N 10.7. ^{1}H NMR (300 MHz, D_2O, 25 °C, pH 7.63): δ = 7.67 (s, 2 H, CH_{arom}), 4.66 (s, 4 H, CH_2OH), 4.02 (d, J = 0.1 Hz, 4 H, CH_2N), 3.09 (s, 4 H, CH_2CH_2), 2.38 (s, 6 H, CH_3) ppm.

Crystals of $[ZnCl(H_2Rpyr_2en)]^+Cl^-\cdot 1.5H_2O$ (1): H_2Rpyr_2en (0.20 g, 0.55 mmol) was dissolved in a mixture of ethanol and water (1:1, 5 mL) containing a few drops of 1 M NaOH, and $Zn(CH_3COO)_2\cdot 2H_2O$ (0.12 g) dissolved in 5 mL of water was slowly added. The pH was adjusted to 7 by addition of a 1 M HCl solution. The mixture was then refluxed at 70 °C for 2 h. No precipitation was observed and the solution was cooled and kept at about 5 °C. After about one month colourless crystals were collected for single-crystal X-ray analysis.

X-ray Crystal Structure Determinations: X-ray data were collected on a Bruker SMART 1000 CCD diffractometer by the φ–ω scan method at room temperature. Reflections were measured for a hemisphere of data with frames covering 0.3° in ω. Of the 7285 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections, 3949 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. Complex scattering factors were taken from the program package SHELXTL.[30] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. The hydrogen atoms were left to refine freely, except the hydrogen atoms H3, H7A, H7B, H7C, H14A, H14B and H14C, which were included in calculated positions and refined in a riding mode. Refinement converged with allowance for thermal anisotropy of all non-hydrogen atoms. Crystal data and details on data collection and refinement are summarized in Table 3.

CCDC-276399 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data collection and refinement parameters.

Formula	$C_{18}H_{29}Cl_2N_4O_{5.5}Zn$
M	525.72
Crystal system	triclinic
Space group	$P\bar{1}$
T [K]	298(2)
a [Å]	9.1208(10)
b [Å]	10.0030(12)
c [Å]	12.3033(14)
α [°]	82.629(2)
β [°]	88.885(2)
γ [°]	89.296(2)
F_{000}	546
Z	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.569
μ [mm^{-1}]	1.383
R_{int}	0.0209
No. measured reflections	7285
No. observed reflections	3949
R_1	0.0522
wR_2 (all data)	0.1516
Largest diff. peak and hole [e Å^{-3}]	0.421 and –1.492

Physical and Spectroscopic Studies: IR spectra were recorded with a BioRad FTS 3000 MX FTIR spectrometer. ^{1}H NMR spectra were recorded with a Varian Unity 300 spectrometer at a probe temperature of about 25 °C.

pH-metric Titration: Protonation and formation constants were determined by pH-metric titration of 25-mL samples. The ionic strength was adjusted to 0.2 M with KCl and the temperature was 25.0 ± 0.1 °C. The ligand concentrations were 0.002 or 0.004 M and the L/M ratios varied from 1 to 4. Titrations were normally carried out from pH 2.2 up to 11.7, with carbonate-free KOH solution of known concentration (ca. 0.2 M) under purified argon. The Zn^{II} stock solution was prepared by dissolving ZnO of *puriss.* quality in excess HCl solution. The Zn^{II} content was determined gravimetrically from the oxinate. The free-acid content was measured by pH-potentiometry. An automatic titration set including a Dosimat 665 autoburette, an Orion 710A precision digital pH-meter and an IBM-compatible computer was used. A Metrohm 6.0234.100 semimicro combined glass electrode was calibrated for hydrogen-ion concentration as described earlier.[31] The pK_w calculated from strong acid–strong base titration was 13.755 ± 0.010. The concentration stability constants, $\beta_{pqr} = [M_pL_qH_r]/[M]_p[L]_q[H]_r$, were calculated with the aid of the computer program PSEQUAD.[25] When referring to stoichiometries of species present in solution, the normal $M_pL_qH_r$ notation is used, where L = Rpyr$_2$en^{2-}.

^{1}H NMR Spectroscopy: All NMR samples were prepared at room temperature immediately before recording the spectra. A quantity of $ZnCl_2$ aqueous solution of known concentration (ca. 0.02 M) was evaporated to dryness and D_2O added and evaporated at least three times to replace the H by D. The samples were prepared in D_2O (99.995% D) by weighing the appropriate amount of ligand and Zn^{II} to give the desired concentration and L/M ratio. The pD values of these solutions were adjusted with DCl and CO_2-free NaOD solutions and measured with a Thermo Orion 420A+ pH-meter with a Mettler Toledo U402-M3-S7/200 combined electrode. The microelectrode was previously calibrated with standard buffered aqueous solutions, and the pH was measured directly in the NMR tubes. The pH-meter readings were converted into pD by using the equation pD = pH + 0.40.[32] Two sets of experiments were performed as a function of pH, with metal-ion concentrations of 4 mM and L/M ratios of 1 and 2. The ^{1}H NMR chemical shifts were referenced relative to DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) at $\delta = 0$ ppm. The signal intensities of the NMR resonances were obtained using the program NUTS.[33]

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