

Total hydrolysis of a new imidazolidine induced by Zn^{II}

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Abstract

2,2'-(2-(2-hydroxyphenyl)imidazolidin-1,3-diyl)diethanol (H₃L) was obtained by condensation between 2-hydroxybenzaldehyde and *N,N'*-bis(2-hydroxyethyl)ethylenediamine. Its potential ability as *NNOOO* donor towards Zn^{II} was tested. This study shows that zinc(II) mediates the fast hydrolysis of H₃L, yielding the free aldehyde and amine. This latter was crystallographically characterised, showing a supramolecular 1D architecture based on hydrogen bond interactions.

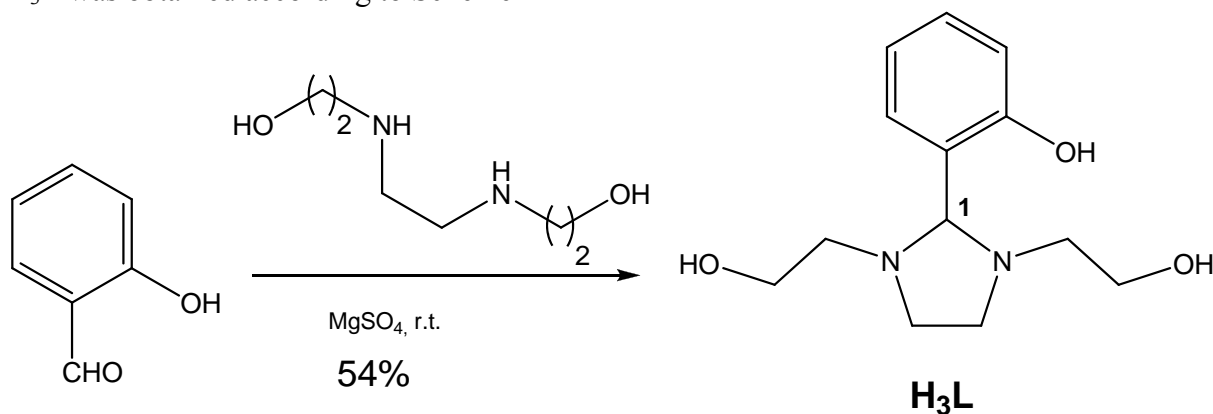
Keywords: imidazolidine / hydrolysis / zinc / 1D ladder

Introduction

Imidazolidines are a well-known class of organic compound of growing interest, due to their numerous pharmaceutical applications, such as anticarcinogenic [1], hypotensor [2] or antibacterial agents [3]. In spite of this, the ability of this kind of donor to bind to metal atoms is still scarcely explored. As a continuation of our studies in the interaction of imidazolidine ligands with *d*-block metal ions [4], we describe herein the synthesis of the H₃L (Scheme 1) and its stability in the presence of Zn^{II}.

Results and discussion

H₃L was obtained according to Scheme 1



Analytical and spectroscopic data corroborate the isolation of the desired compound, with formation of the imidazolidine ring. Thus, H1 and C1 atoms (Scheme 1) appear in the ¹H and ¹³C NMR spectra at 3.81 ppm (singlet) and 88.9 ppm, respectively, and the mass spectrum (ESI) shows the molecular peak at *m/z* 251 (M-H).

The reaction of H₃L towards Zn(OAc)₂ was tested. This reaction leads to a yellow oil, whose spectroscopic characterisation clearly shows that the ligand suffers hydrolysis. Thus, the oil is really a mixture, composed of the free zinc acetate, amine and aldehyde (Figure 1). These species could be unequivocally identified by comparison of the ¹H NMR spectrum of the oil with those of the free compounds. In this way, it should be noted that the hydrolysis of the ligand is clearly demonstrated by the presence of a new singlet at 9.86 ppm and the total absence of the singlet at 3.81 ppm, corresponding to H1.

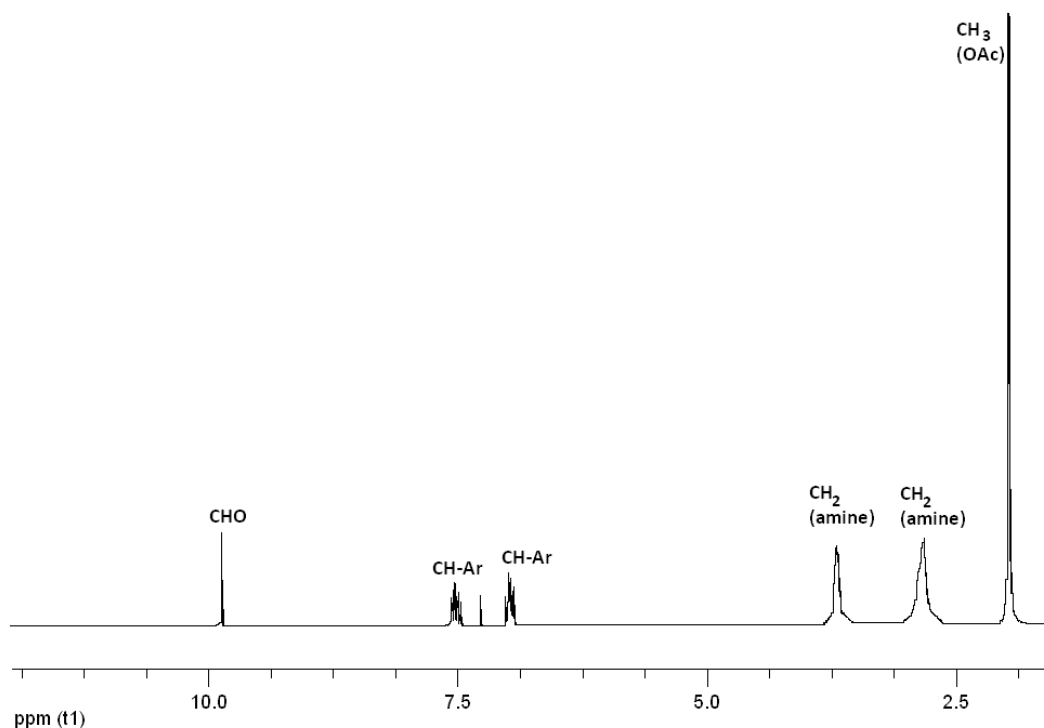


Fig. 1. ^1H NMR spectrum of the oil in CDCl_3

This result indicates that the presence of the 2-hydroxyethyl residues makes extremely labile the C1-N bond in H_3L . This can be stated because many zinc complexes with similar ligands, lacking 2-hydroxyethyl groups, have been previously isolated without any evidence of hydrolysis [5].

The hydrolysis of H_3L and the presence of the free amine in the oil mixture could also be unequivocally established by single X-ray diffraction studies. Thus, the free amine was isolated from the mixture in the form of single crystals. A perspective view of the molecule is shown in Figure 2. All the angles and distances are in the range of those expected for this kind of compound and do not deserve further consideration. Therefore, just to note that the amine has an inversion centre in the middle of the molecule, being both halves equivalent.

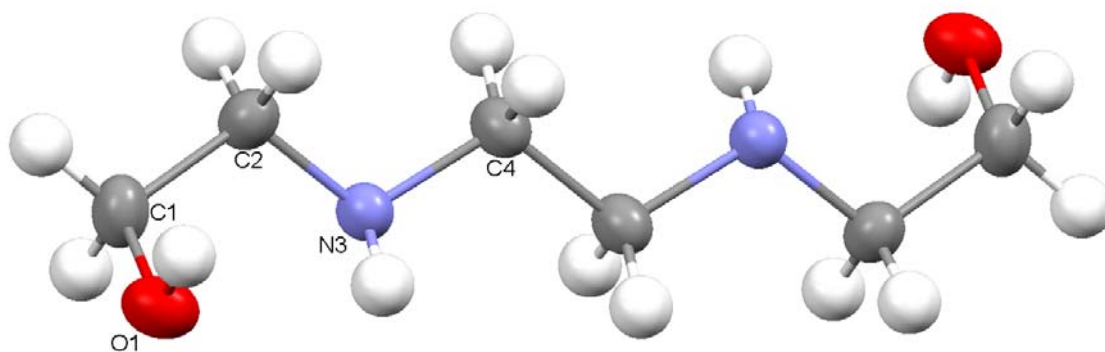


Fig. 2. Ellipsoid diagram for H_3L . Only the non-H atoms of the asymmetric unit are labelled.

In addition, it is remarkable that both the amine and hydroxyl groups are involved in hydrogen bonds. These interactions expand the initial molecule into a 1D solid. Thus, the overall structure of the amine can be described as a supramolecular ladder (Figure 3).

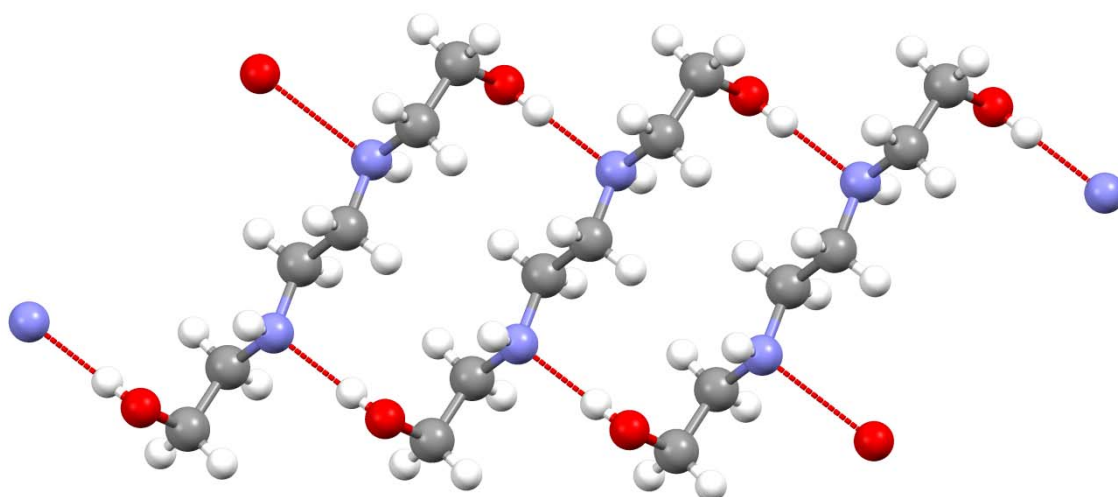


Fig. 3. Hydrogen bond scheme for H₃L

Conclusions

The new imidazolidine derivative H₃L was prepared with high yield and purity. The reactivity of the organic compound towards Zn^{II} shows that the C1-N bond is extremely unstable in the occurrence of this metal ion, suffering complete hydrolysis. This process leads to a mixture of 2-hydroxybenzaldehyde, *N,N'*-bis(2-hydroxyethyl)ethylenediamine and the zinc(II) salt. The high instability of this bond is associated with the presence of the 2-hydroxyethyl residue.

The X-ray structure of the free amine, obtained from the final crude of the reaction, shows an extended hydrogen bond scheme that expands the initial amine node into an infinite ladder.

Experimental

Synthesis of H₃L

H₃L was isolated as follows: to a solution of 2-hydroxybenzaldehyde (4.72 ml, 64 mmol) in absolute ethanol (200 mL), *N,N'*-bis(2-hydroxyethyl)ethylenediamine (9.61 g, 64.84 mmol) and MgSO₄ were added. The resultant suspension was stirred at room temperature for 16 h. and then filtered. The obtained oil was purified by recrystallisation in ethylacetate, giving rise to H₃L (8.65 g, 54 %), as yellow crystals. m.p.: 83–88 °C. Elemental analysis: found: C, 61.76; H, 8.47; N, 11.21; calcd. for C₁₃H₂₀N₂O₄ C, 61.90; H, 7.93; N, 11.21. ¹H-RMN (250 Hz, CDCl₃) δ: 7.20 (dt, *J* = 1.8 and 8.0 Hz, 1H, ArH), 6.96 (dd, *J* = 1.5 and 7.8 Hz, 1H, ArH), 6.80 (m, 2H, 2×ArH), 3.81 (s, 1H, CH), 3.63–3.42 (m, 6H, 3×CH₂), 2.79 (m, 2H, CH₂), 2.60 (m, 2H, CH₂) and 2.39 (td, *J* = 4.1 and 12.5 Hz, 2H, CH₂) ppm. ¹³C-RMN (63 MHz, CDCl₃) δ: 157.7 (C), 130.8 (CH), 130.2 (CH), 120.8 (C), 118.9 (CH), 116.9 (CH), 88.9 (CH), 59.8 (2×CH₂), 54.0 (2×CH₂) and 49.9 (2×CH₂) ppm. IR (ATR, ν/cm⁻¹): 3404 (b), 3500 (sh) (OH). MS (ESI-) *m/z* found, 251.1385; calcd. for C₁₃H₂₀O₃N₂ (M–H).

Reaction of H₃L with Zn^{II}

To a solution of H₃L (0.05 g, 0.2 mmol) in acetonitrile (10 mL), a solution of Zn(OAc)₂·4H₂O (0.087 g, 0.4 mmol) was added. The resultant solution was stirred at room temperature for 1 h. and concentrated to dryness. The obtained yellow oil was characterised by ¹H NMR spectroscopy. ¹H-RMN (250 Hz, CDCl₃) δ: 9.86 (s, 1H, CHO), 7.55–7.46 (m, 2H, ArH), 7.01–6.93 (m, 2H, ArH), 3.76–3.63 (m, CH₂), 2.74–2.73 (m, CH₂), 1.93 (s, CH₃-OAc) ppm.

Attempts of recrystallisation of the crude oil in ethylacetate yield single crystals of *N,N'*-bis(2-hydroxyethyl)ethylenediamine, suitable for X-ray diffraction studies. Crystal data: (at 100(2) K): monoclinic, *P*2₁/*n*, C₆H₁₆N₂O₂, *MW* = 148.21, with *a* = 9.944(5) Å, *b* = 8.778(54) Å, *c* = 18.967(5) Å and β = 92.306(5), *V* = 398.77(7) Å³, *Z* = 2; *R*₁ = 0.0326 and *wR*₂ = 0.0846 (*I* > 2σ*I*).

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