

Schiff base hydrolysis mediated by d-block metals

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Abstract

Condensation of imidazol-2-carboxaldehyde and 2-tosylaminomethylaniline (HL^{Ts}) in ethanol under reflux yields the Schiff base H_2L . The interaction of this Schiff base with palladium(II), cadmium(II) or zinc(II) acetates in 1:1 molar ratio was investigated. This study demonstrates that the expected Schiff base metal complexes cannot be isolated. Instead, chemical synthesis starting from metal acetates leads to the products $Pd(L^{Ts})_2 \cdot 2H_2O$, $Cd(L^{Ts})_2$ and $Zn(L^{Ts})_2$, as a result of the Schiff base hydrolysis.

Keywords: Schiff base, hydrolysis, zinc, cadmium, palladium

Introduction

Schiff bases are a kind of versatile ligands which are readily synthesized from the reaction of primary amines with carbonyl containing compounds. Metal complexes with this kind of ligand have attracted considerable interest because they are widely applied as versatile catalyst systems¹ and components of materials with interesting supramolecular, magnetic and photophysical properties.^{1e,2} Recently, we began to work with a specific kind of Schiff base, derived from 2-tosylaminomethylaniline and different aldehydes. The study of d-block metal complexes containing this type of donor has produced some interesting results, such as ring/chain tautomerism induced by the presence of certain metal ions,³ or metal-mediated aerobic oxidation of methanol.⁴ Thus, as a continuation of this work, we describe herein the synthesis and characterisation of a new Schiff base (H_2L) derived from imidazol-2-carboxaldehyde and 2-tosylaminomethylaniline and its behaviour towards Pd^{II} , Cd^{II} and Zn^{II} .

Experimental

Ligands and complexes were obtained as summarised in Sch. 1 and as detailed below.

Synthesis of the ligands

HL^{Ts} was prepared by a method previously described.⁵

H_2L . A solution of imidazol-2-carboxaldehyde (0.14 g, 1.45 mmol) and 2-tosylaminomethylaniline (0.40 g, 1.45 mmol) in ethanol (40 mL) was refluxed for 30 min. The solution was concentrated in a rotaevaporator until a pale yellow solid precipitated. The solid was filtered and the crude was purified by column chromatography, using a mixture of ethylacetate:diethylether (1:3) as eluent. Purification is followed by thin-layer chromatography, the first fraction of the solution containing the Schiff base ligand. Concentration of this solution gave rise to a white solid, which was filtered and dried in air. Yield = 0.42 g (83%). Mp = 134 °C. ¹H NMR (500 MHz, DMSO-*d*₆, δ): 12.91 (s, 1H, HN_{imidazol}), 8.21 (s, 1H, H14), 7.89 (t, 1H, $J = 6.4$ Hz, HNSO₂), 7.62 (d, 2H, $J = 8.2$ Hz, H3 + H5), 7.40 (d, 1H, $J = 8.4$ Hz, H16), 7.32 (d, 1H, $J = 8.4$ Hz, H9), 7.29-7.26 (m, 3H, H2 + H6 + H11), 7.19-7.14 (m, 2H, H12 + H17), 7.05 (d, 1H, H12), 4.14 (d, 1H, H7), 2.33 (s, 3H, H40) ppm. MS (MALDI-TOF⁺) m/z (%): 354.9 (100) [H_2L+H]⁺. Elemental analysis: C 60.3; H 5.0; N 15.6; S 8.7%; calculated for C₁₈H₁₈N₄O₂S: C 60.9; H 5.1; N 15.8; S 9.1%.

Slow evaporation of an ethanol solution of H₂L yields crystals, suitable for single X-ray diffraction studies. Crystal data for H₂L (at 293 K): monoclinic, *P*2₁, C₁₈H₁₈N₄O₂S, *MW* = 354.42, *a* = 9.8185(8), *b* = 5.0754(4), *c* = 17.0145(13) Å, β = 92.772(5), *V* = 846.89(12) Å³, *Z* = 2, *R*₁ = 0.0355 and *wR*₂ = 0.0791 (*I* > 2σ*I*).

Synthesis of metal complexes

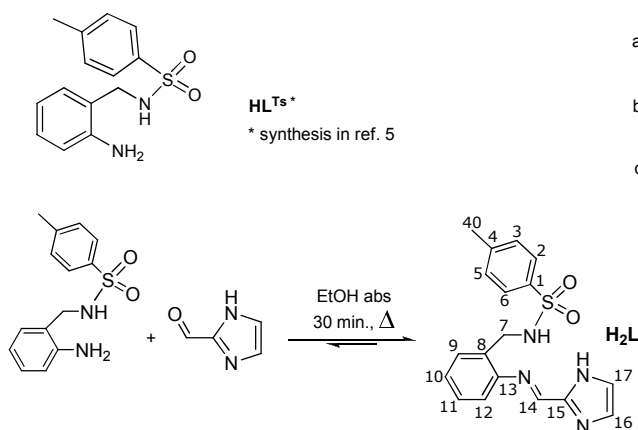
Pd(L^{Ts})₂·2H₂O, Cd(L^{Ts})₂ and Zn(L^{Ts})₂ were prepared by a chemical method exemplified by the isolation of Pd(L^{Ts})₂·2H₂O.

Pd(L^{Ts})₂·2H₂O: To a solution of H₂L (0.05 g, 0.14 mmol) in methanol (50 mL) Pd(OAc)₂·4H₂O (0.033 g, 0.14 mmol) was added. The mixture was stirred for 20 min. at room temperature, precipitating a grey powder, which was collected by filtration and dried in air. Yield 0.06 g (62%). ¹H NMR (500 MHz, DMSO-*d*₆, δ): 7.51 (d, *J* = 8.12 Hz, 4H, H2 + H6), 7.03-6.95 (m, 10H, H3 + H5 + H10 + NH₂), 6.90-6.82 (m, 4H, H11 + H12), 6.79 (d, *J* = 7.62 Hz, 2H, H9), 4.03 (s, 4H, H7), 2.23 (s, 6H, H40). IR. MS (MALDI-TOF) *m/z* (%): 655.9 (100) [Pd(L^{Ts})₂ + H]⁺. Elemental analysis: C 48.9; H 4.5; N 8.3; S 9.2; calculated for C₂₈H₃₂N₄O₆S₂Pd: C 48.6; H 4.6; N 8.1; S 9.3.

Zn(L^{Ts})₂: Yield: 0.06 mg (69%). ¹H NMR (500 MHz, DMSO-*d*₆, δ): 7.49 (d, *J* = 7.6 Hz, 4H, H2 + H6), 7.14-6.93 (m, 16H, H3 + H5 + H10 + H11 + H12 + NH₂), 3.96 (s, 4H, H7), 2.20 (s, 6H, H40) ppm. MS (MALDI-TOF) *m/z* (%): 617.1 (100) [Zn(L^{Ts})₂ + H]⁺. Elemental analysis C 54.6; H 4.9; N 9.1; S 10.4; calculated for C₂₈H₃₀N₄O₄S₂Zn: C 55.0; H 4.6; N 9.5; S 10.0.

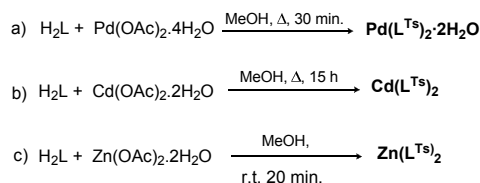
Cd(L^{Ts})₂: Yield: 0.034 g (39%). ¹H NMR (500 MHz, DMSO-*d*₆) δ: 7.64 (d, *J* = 8.11 Hz, 4H, H2 + H6), 7.23-7.04 (m, 16H, H3 + H5 + H10 + H11 + H12 + NH₂), 4.04 (s, 4H, H7), 2.25 (s, 6H, H40). MS (MALDI-TOF) *m/z* (%): 664.1(100) [Cd(L^{Ts})₂ + H]⁺. Elemental analysis C 51.3; H 4.1; N 8.2; S 9.5; calculated for C₂₈H₃₀N₄O₄S₂Cd: C 50.72; H 4.56; N 8.45; S 9.7.

Synthesis of HL^{Ts} and H₂L



Sch. 1. Synthetic routes for HL^{Ts}, H₂L and metal complexes, with numbering scheme for NMR characterisation

Synthesis of metal complexes



Results and discussion

The condensation of imidazol-2-carboxaldehyde and 2-tosylaminomethylaniline allows isolating H₂L (Sch. 1) with high yield and purity. Its reaction with palladium(II), cadmium(II) or zinc(II) acetates efficiently promote the hydrolysis of the ligand, giving rise to pure amine complexes. The temperature does not seem to play a fundamental role in the hydrolysis process, as the zinc amine complex can be obtained at room temperature or at reflux.

All the compounds were unequivocally identified by a combination of elemental analysis, mass spectrometry and ^1H NMR spectroscopy techniques. H_2L could also be crystallographically characterised.

X-ray diffraction studies

An ORTEP view of H_2L is shown in Fig. 1. All distances and angles are within the expected range and do not deserve further consideration. However, it is noteworthy that each discrete molecule interacts with two neighbouring units by hydrogen bond (Fig. 2), so expanding the initial ligand block into a chain.

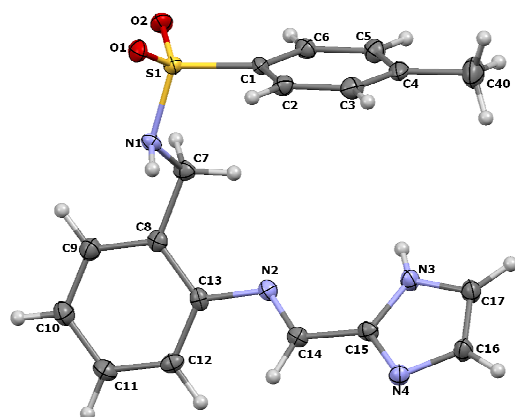


Fig. 1. Molecular structure of H_2L

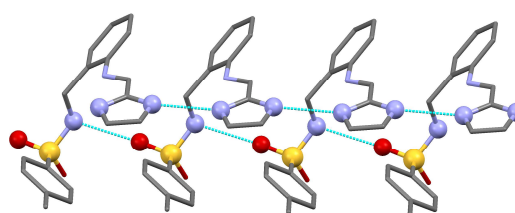


Fig. 2. Hydrogen bond scheme for H_2L

Spectroscopic characterisation

The 6.9-8.5 ppm region of the ^1H NMR spectrum of H_2L is shown in Fig. 3. The spectrum presents all the expected signals (see experimental and Sch. 1) and agrees with the presence of a unique species in solution and with its high purity.

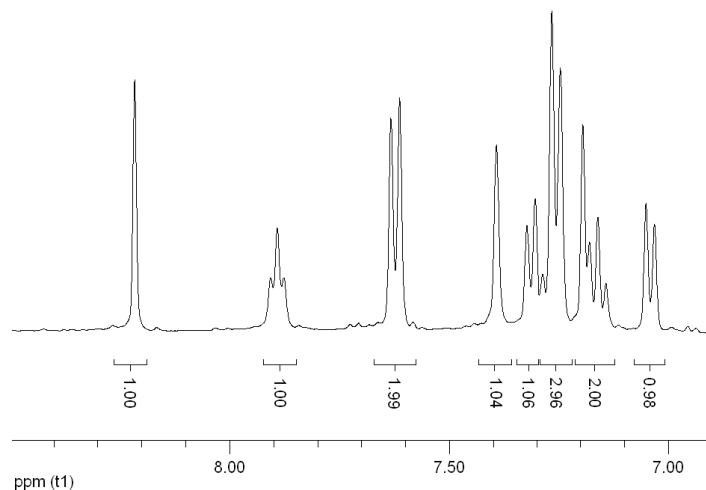


Fig. 3. ^1H NMR spectrum of H_2L in the 6.9-8.5 ppm range in $\text{dmsO}-d_6$

The ^1H NMR spectra of all the complexes also clearly show the clean hydrolysis process of the Schiff base, which allows to isolate $\text{M}(\text{L}^{\text{Ts}})_2$ complexes as the only species, as it is exemplified by the aromatic region of the spectrum of $\text{Pd}(\text{L}^{\text{Ts}})_2 \cdot 2\text{H}_2\text{O}$, shown in Fig. 4.

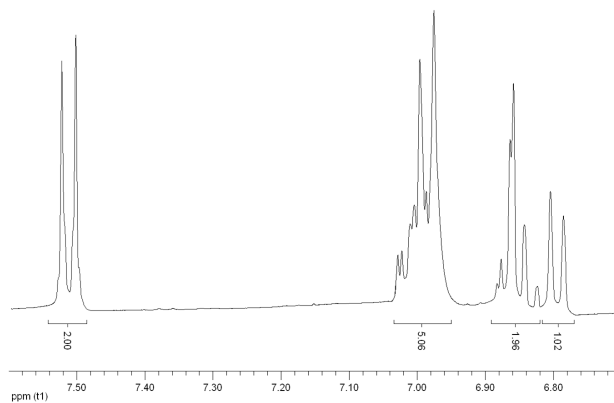


Fig. 4. ^1H NMR spectrum of $\text{Pd}(\text{L}^{\text{Ts}})_2 \cdot 2\text{H}_2\text{O}$ in the 6.7-7.6 ppm range in $\text{dmsO}-d_6$

Mass spectra further confirm the absence of complexes containing the Schiff base ligand. All the mass spectra contain the $[\text{M}(\text{L}^{\text{Ts}})_2 + \text{H}]^+$ peak as the molecular one, with any other peak of significant intensity, as it can be shown for the spectrum of $\text{Zn}(\text{L}^{\text{Ts}})_2$ in Fig. 5.

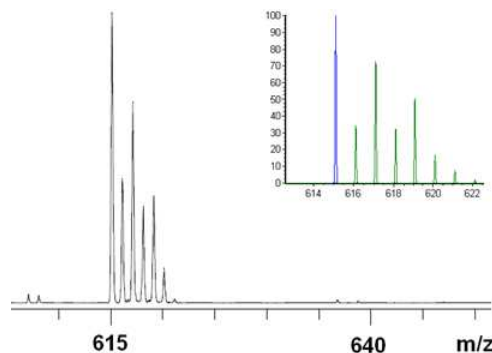


Fig. 5. Partial view of the mass spectrum (MALDI-TOF) of $\text{Zn}(\text{L}^{\text{Ts}})_2$, showing the molecular peak. Inset: calculated isotopic distribution

Conclusions

The presence of palladium(II), cadmium(II) or zinc(II) in a solution of H_2L promotes the hydrolysis of the ligand, yielding complexes of formula $\text{M}(\text{L}^{\text{Ts}})_2 \cdot n\text{H}_2\text{O}$ ($n = 2$ or 0) as pure products. No evidence of the Schiff base metal complexes was detected, showing the high efficiency of these metal ions in the hydrolysis of the imine bond in this kind of Schiff base.

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