A simple route to dinuclear complexes of a sulfonamide ligand with a potential interest in the catalysis field

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Abstract: We report here the straightforward synthesis of some *d*-block metal dimers of a Schiff base ligand obtained by condensation of 2-tosylaminomethylaniline with 4-formyl-3-hydroxybenzoic acid (H_2L). The easy bideprotonation of both -OH and -$HNSO_2$- groups, as well as a suitable *N,N,O* binding domain that can simultaneously bind two metal ions through μ_2-$N_{\text{sulfonamido}}$ bridges have been considered during the design step of the Schiff base ligand. All the compounds synthesised were characterised by a combination of mass spectrometry, infrared spectroscopy, elemental analysis and, when applicable, by ^{1}H NMR spectroscopy. We have used NOESY experiments for structure elucidation of H_2L and $(NH_4)_2[Pd_2L_2]\cdot 2H_2O$ in solution.

Keywords

Dinuclear complexes / *d*-block metals / Schiff bases / enolimines

Introduction

Our research efforts to synthesise dinuclear metal complexes of sulfonamide ligands with a potential interest in the catalysis field arises from the reported use of $Zn_2L_2Et_2$ (Fig. 1) as an efficient catalyst in the synthesis of poly(*L*-lactide)-Vitamin E TPGS nanoparticles (TPGS = tocopheryl polyethylene glicol succinate) [1]. One might note that the tridentate Schiff base ligand used to obtain $Zn_2L_2Et_2$ derives from the mono-condensation of a salicylaldehyde derivative and 2-tosylaminobenzylamine, which has been first synthetised by us [2].

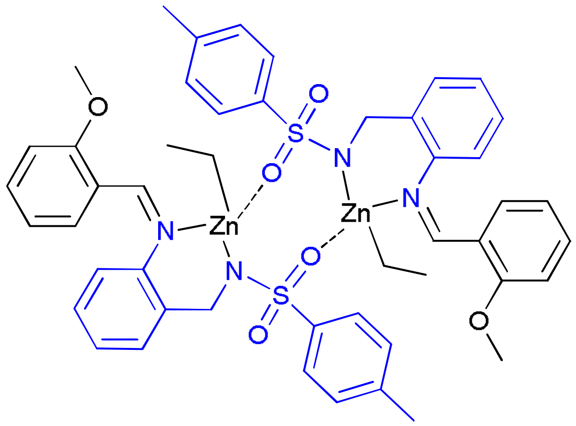
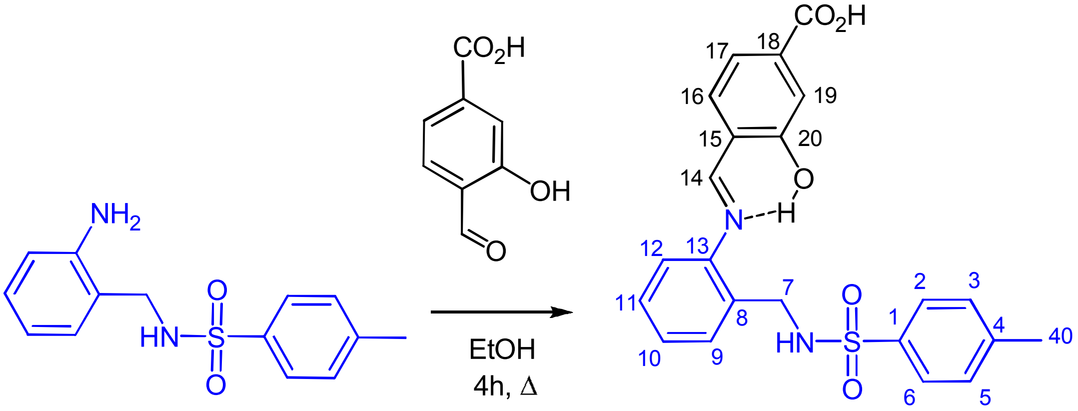


Fig. 1. Proposed structure [1] for $Zn_2L_2Et_2$ with the 2-tosylaminobenzylamine residue highlighted in blue colour.

With the aim of synthesising dinuclear metal complexes of sulfonamide ligands, we have designed a monotopic Schiff base ligand (scheme 1), which derives from the reaction of 2-tosylaminobenzylamine [2] with 4-formyl-3-hydroxybenzoic acid (H_2L). The easy bideprotonation of both -OH and -$HNSO_2$- groups, as well as a suitable *N,N,O* binding domain that can simultaneously bind two metal ions through μ_2-$N_{sulfonamido}$ bridges have been considered during the design step.



Scheme 1. Schematic representation of the synthesis of H_2L, showing the numbering scheme for NMR studies.

Material and methods

Synthesis of H_2L

H_2L could be obtained after cooling at room temperature an absolute ethanol solution (40 mL) containing 4-formyl-3-hydroxybenzoic acid (0.09 g, 0.55 mmol) and 2-

tosylaminomethylaniline [2] (0.15 g, 0.55 mmol) that had been refluxing for 4 hours. The pale yellow precipitate formed was separated and air-dried.

Yield = 0.21 g (92%). Mp = 134 °C. ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 13.03 (s, 1H, HOCO), 12.33 (s, 1H, HO20), 8.79 (s, 1H, H14), 8.00 (t, 1H, HN), 7.78 (d, 1H, H16), 7.63 (d, 1H, H2 + H6), 7.51 (d, 1H, H17), 7.46 (s, 1H, H19), 7.38 (d, 1H, H9), 7.36 (t, 1H, H11), 7.29 (d, 2H, H3 + H5), 7.28 (t, 1H, H10), 7.21 (d, 1H, H12), 4.08 (d, 2H, H7), 2.34 (s, 3H, H40). ^{13}C NMR (125 MHz, DMSO-d_6, δ en ppm): 167.1(COOH), 162.6 (C14), 147.6 (C13), 132.2 (C16), 129.8 (C3 + C5), 129.1 (C9), 129.0 (C11), 127.0 (C2 + C6), 120.0 (C17), 119.5 (C10), 119.0 (C12), 117.6 (C19), 42.6 (C7), 21.5 (C40). IR (KBr, ν/cm^{-1}): ν(OH) 3442, ν(OH) 3315, ν(C=N$_{\text{imine}}$) 1695, ν_{as}(SO$_2$) 1329, ν_s(SO$_2$) 1151. MS (ESI$^+$, MeOH/HCOOH) *m/z*: 425.2 [H$_2$L + H]$^+$. Elemental Analysis: C 61.9; H 4.8; N 6.6; S 7.5%; calc. for $C_{22}H_{20}N_2O_5S$: C 62.3; H 4.8; N 6.6; S 7.6%.

Syntheses of the complexes

$(NH_4)_2[Pd_2L_2]\cdot 2H_2O$

A methanol solution (20 mL) of H$_2$L (0.10 g, 0.24 mmol) was added to other methanol solution (20 mL) of Pd(OAc)$_2$ (0.05 g, 0.24 mmol), and then 2 drops of an aqueous solution of NH$_3$ (17%) This mixture was refluxed for 4h 30 min to yield a suspension that was filtered off, washed with warm methanol (10 mL) and then air-dried.

Yield: 0.14 g (52%). ^{1}H RMN (500 MHz, DMSO-d_6, δ /ppm): 8.12 (s, 2H, H14), 7.61 (d, 2H, H16), 7.58 (d, 4H, H2 + H6), 7.34 (s, 2H, H19), 7.12 (d+t, 4H, H9+H11), 7.07 (t+d, 4H, H10+H17), 6.88 (d, 4H, H3+H5), 6.84 (d, 2H, H12), 4.14 (d, 4H, H7), 3.66 (s, 8H, NH$_4^+$), 2.18 (s, 6H, H40). ^{13}C RMN (125 MHz, DMSO-d_6, δ/ppm): 167.6 (COO), 164.2 (C20), 162.7 (C14), 144.9 (C13), 142.5 (C1), 139.8 (C4), 137.6 (C18), 137.1 (C16), 133.4 (C8), 129.5 (C10), 128.8 (C9), 128.3 (C3 + C5), 126.8 (C11), 126.1 (C2+C6), 123.7 (C15), 121.7 (C12), 121.5 (C19), 114.9 (C17), 50.2 (C7), 21.2 (C40). IR (KBr, ν/cm^{-1}): ν(OH$_w$) 3436, ν(NH$_4^+$) 3372, 3340, ν(COO) 1724, ν(C=N) 1607, ν_{as}(SO$_2$) 1384, ν_s(SO$_2$) 1134. Elemental analysis: C 47.1; H 4.2; N 7.5; S 5.7%; calc. for $C_{44}H_{46}N_6O_{12}Pd_2S_2$: C 46.9; H 4.1; N 7.5; S 5.7%.

$Zn_2L_2·4H_2O$

The zinc complex has been obtained by electrochemical oxidation of a metal anode immersed in an acetonitrile solution (80 mL) of H_2L (0.05 g, 0.12 mmol), containing tetraethylammonium perchlorate (ca. 50 mg) as supporting electrolyte (***Caution:*** *Although no problem has been encountered in this work, all perchlorate compounds are potentially explosive and should be handled in small quantities and with great care!*). This was electrolysed for about 1h and 25 min at a current intensity of 5.0 mA and an initial voltage of 5 V. The resulting yellow precipitate was filtered off, washed with acetonitrile (10 mL) and then air-dried.

Yield: 0.10 g (80%). MS (MALDI-TOF$^+$, DCTB) *m/z*: 977.1 $[Zn_2L_2+H]^+$. IR (KBr, ν/cm^{-1}): ν(O-H$_w$) 3436, ν(O-H) 3280, ν(C=O) 1697, ν(C=N) 1614, $\nu_{as}(SO_2)$ 1326, $\nu_s(SO_2)$ 1158. Elemental analysis: C 50.1; H 4.6; N 5.1; S 5.9%, calc. for $C_{44}H_{44}N_4O_{14}S_2Zn_2$: C 50.4; H 4.2; N 5.4; S 6.1%.

$Co_2L_2·4H_2O$

The cobalt complex has been obtained by electrochemical oxidation of a metal anode immersed in an acetonitrile solution (60 mL) of H_2L (0.05 g, 0.12 mmol), containing tetraethylammonium perchlorate (ca. 50 mg) as supporting electrolyte (***Caution:*** *Although no problem has been encountered in this work, all perchlorate compounds are potentially explosive and should be handled in small quantities and with great care!*). This was electrolysed for about 1h and 25 min at a current intensity of 5.1 mA and an initial voltage of 5 V. The resulting brown precipitate was filtered off, washed with acetonitrile (20 mL) and then air-dried.

Yield: 0.04g (61%). MS (MALDI-TOF$^+$, DCTB) *m/z*: 963.1 $[Co_2L_2+H]^+$. IR (KBr, ν/cm^{-1}): ν(O-H$_w$) 3435, ν(C=N) 1613, $\nu_{as}(SO_2)$ 1324, $\nu_s(SO_2)$ 1159. Elemental analysis: C 50.9; H 4.1; N 5.3; S 6.0%, calc. for $C_{44}H_{44}Co_2N_4O_{14}S_2$: C 51.1; H 4.3; N 5.4; S 6.2%.

$Ni_2L_2·4H_2O$

The nickel complex has been obtained by electrochemical oxidation of a metal anode immersed in an acetonitrile solution (60 mL) of H_2L (0.05 g, 0.12 mmol), containing tetraethylammonium perchlorate (ca. 50 mg) as supporting electrolyte (***Caution:*** *Although no problem has been encountered in this work, all perchlorate compounds are potentially explosive and should be handled in small quantities and with great care!*).

This was electrolysed for about 1h and 25 min at a current intensity of 5.1 mA and an initial voltage of 5 V. The resulting brown precipitate was filtered off, washed with acetonitrile (20 mL) and then air-dried.

Yield: 0.04g (60%). MS (MALDI-TOF$^+$, DCTB) *m/z*: 963.2 $[Ni_2L_2+H]^+$. IR (KBr, v /cm^{-1}): v(O-H$_w$) 3430, v(C=N) 1618, v_{as}(SO$_2$) 1323, v_s(SO$_2$) 1159. Elemental analysis: C 51.4; H 4.5; N 5.6; S 6.1%, calc. for $C_{44}H_{44}N_4Ni_2O_{14}S_2$: C 51.1; H 4.3; N 5.4; S 6.2%.

Physical measurements

The free ligand and its complexes were characterised by a combination of elemental analysis, infrared spectroscopy, mass spectrometry and, when applicable, by ^{1}H NMR spectroscopy.

Elemental analyses of C, H and N were performed on a Carlo Erba EA 1108 analyzer. IR spectra were recorded as KBr pellets on a FT-IR Mattson Instruments 202Q spectrophotometer in the range 4000-600 cm^{-1}. MALDI-TOF mass spectra were recorded on a Bruker Ultraflex III TOF/TOF using methanol as solvent and DCTB as matrix. ^{1}H NMR spectra were recorded on a Bruker DPX-250 spectrometer using DMSO-d_6 as solvent.

Results and discussion

H_2L

The Schiff base ligand, along with negligible amounts of the ring tautomer (tetrahydroquinazoline), has been synthesised *via* nucleophilic addition of 2-tosylaminomethylaniline [2] to 4-formyl-3-hydroxybenzoic acid.

The 2-D NOESY spectrum of H_2L (Fig. 2) shows cross peaks due to the coupling of the imine proton (H-14, at about 8.8 ppm) with aromatic protons H-12 (at about 7.2 ppm) and H-16 (at about 7.8 ppm). The results of the NOESY experiment allow elucidating the conformation adopted by H_2L in solution, which is shown in Scheme 1. The *E* configuration displayed by the enolimine tautomer is favoured by an intramolecular H-bond between the 2-hydroxyl substituent and the -HC=N- group. The strength of this bond appears to be the cause for the stabilisation of the enolimine form [3].

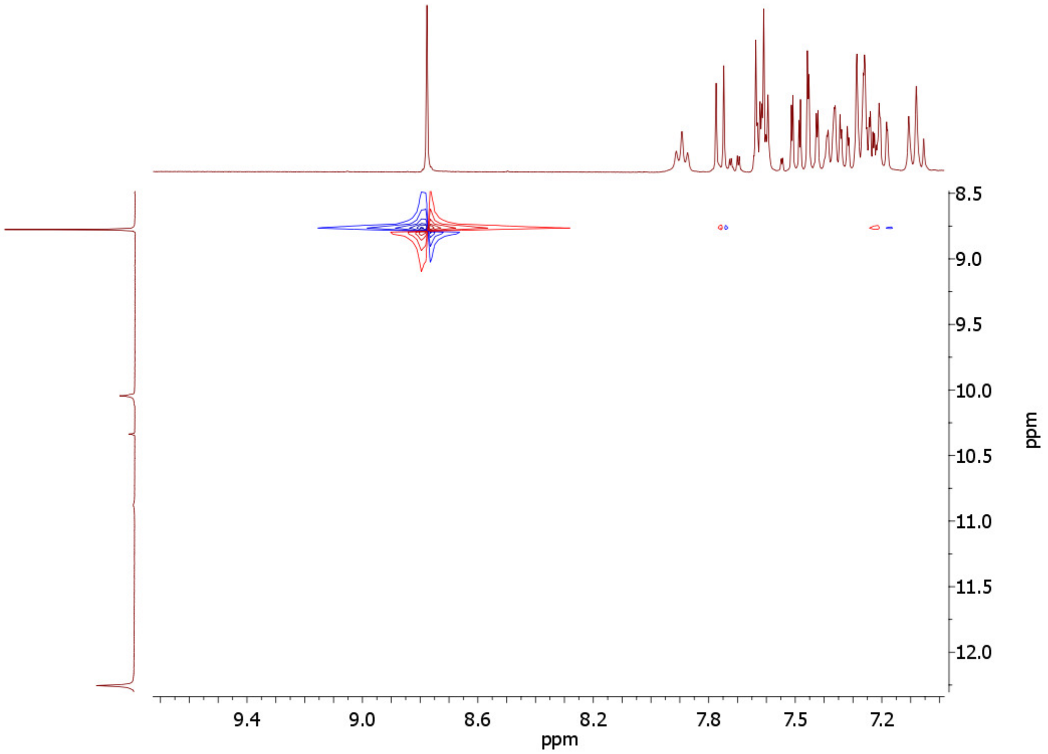


Fig. 2. Partial view of the NOESY spectrum of H_2L showing the coupling of the imine proton (H-14, at about 8.8 ppm) with aromatic protons H-12 (at about 7.2 ppm) and H-16 (at about 7.8 ppm).

Metal complexes.

$(NH_4)_2[Pd_2L_2]\cdot 2H_2O$ has been synthesised in low yield by reaction of $Pd(OAc)_2$ with H_2L in the presence of two drops of an aqueous solution of NH_3. With the aim of synthesising dinuclear metal complexes of sulfonamide ligands with higher yields, we have investigated the use of an electrochemical method for the synthesis of some *d*-block metal complexes. As a result $Zn_2L_2\cdot 4H_2O$, $Co_2L_2\cdot 4H_2O$ and $Ni_2L_2\cdot 4H_2O$ have been synthesised. These complexes could be characterised by a combination of mass spectrometry, infrared spectroscopy, elemental analysis, and, when applicable, by ^1H NMR spectroscopy.

MALDI-TOF mass spectra of the complexes have evidenced their dinuclear nature, being possible the identification of intense signals assignable to molecular ions of the type $[M_2L_2 + H]^+$. Fig. 3 shows a partial view of the MALDI-TOF mass spectra of $Ni_2L_2\cdot 4H_2O$ and $Co_2L_2\cdot 4H_2O$. Basing on the reported crystal structure of $Cu_2L_2\cdot 2MeCN$ [4], we propose here that the repeating units are held together by μ-$N_{sulfonamido}$ bridges between the metal centres rather than by M-O_{tosyl} bonds. The type of link here proposed has been already found in dinuclear metal complexes of sulfonamide ligands involved in catalysis [5].

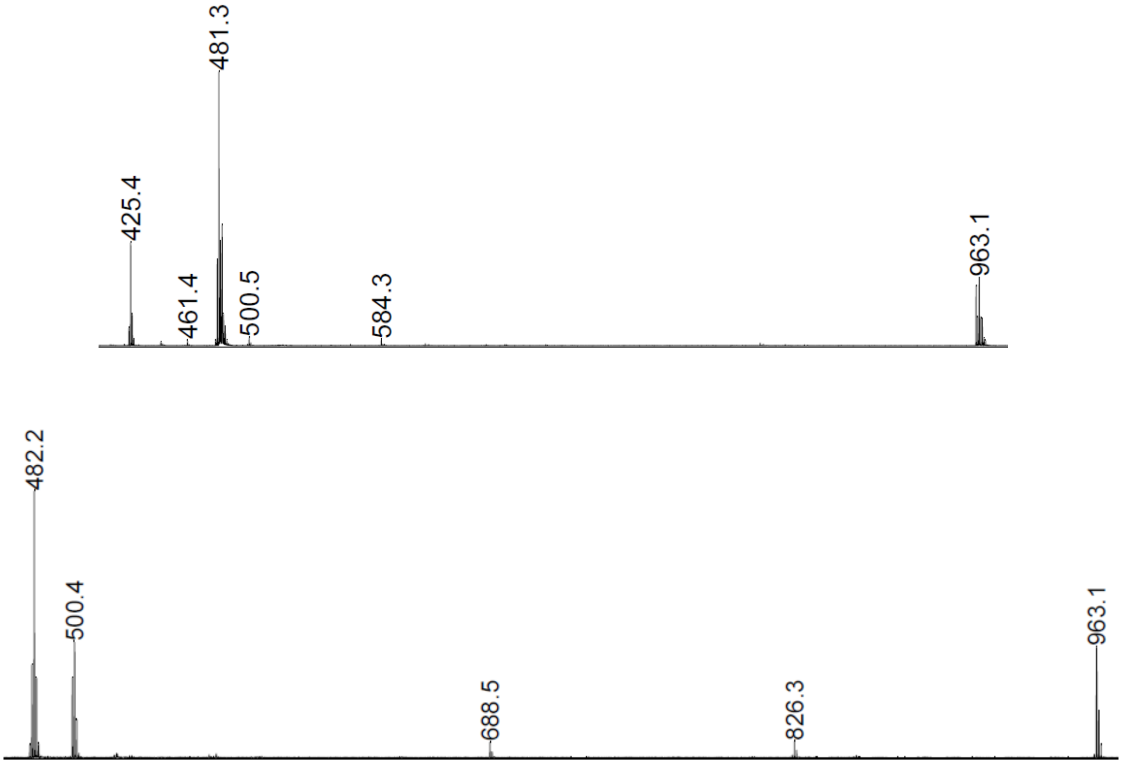


Fig. 3. Partial view of the MALDI-TOF mass spectra of $Ni_2L_2{\cdot}4H_2O$ (top) and $Co_2L_2{\cdot}4H_2O$·(bottom) in DCTB.

Fig. 4 shows the ^{1}H NMR spectrum of $(NH_4)_2[Pd_2L_2]{\cdot}2H_2O$. Since the spectrum of $(NH_4)_2[Pd_2L_2]{\cdot}2H_2O$ evidencing homotopic methylene protons in dmso-d_6 (δ about 4.1 ppm), we have assumed that the two methylene protons can interconvert easily by fast change in the envelope conformation of six-membered metallacycles of aniline residues, becoming H7 protons equivalent.

The 2-D NOESY spectrum of $(NH_4)_2[Pd_2L_2]{\cdot}2H_2O$ shows cross peaks due to the coupling of the imine proton (H-14) with aromatic protons H-12 and H-16 (Fig. 5, blue line). In view of the rigidity of $(NH_4)_2[Pd_2L_2]{\cdot}2H_2O$, these couplings allow elucidating its conformation in solution, which is shown in Fig. 4 (inset).

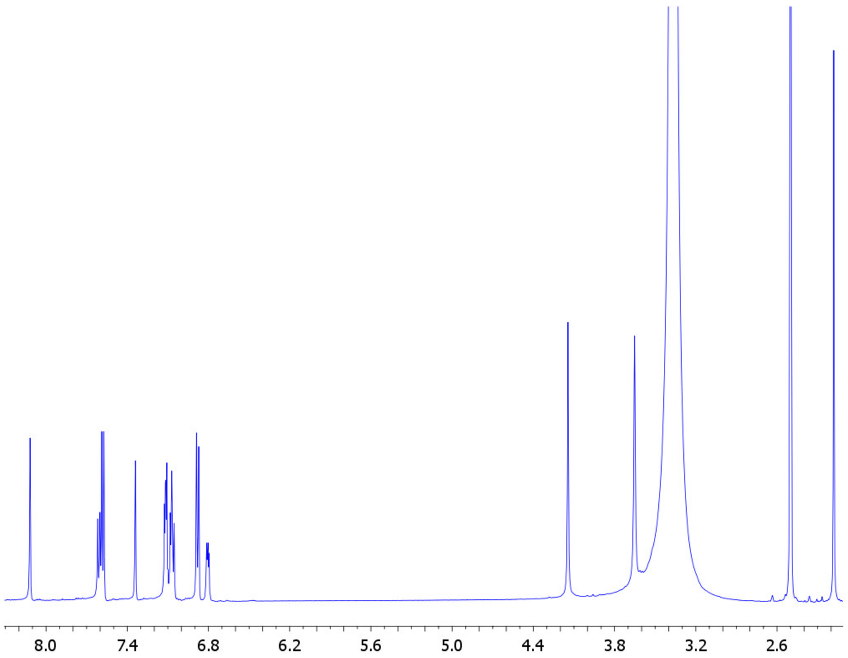


Fig.4. ^{1}H NMR spectrum of $(NH_4)_2[Pd_2L_2]\cdot 2H_2O$ in dmso-d_6.

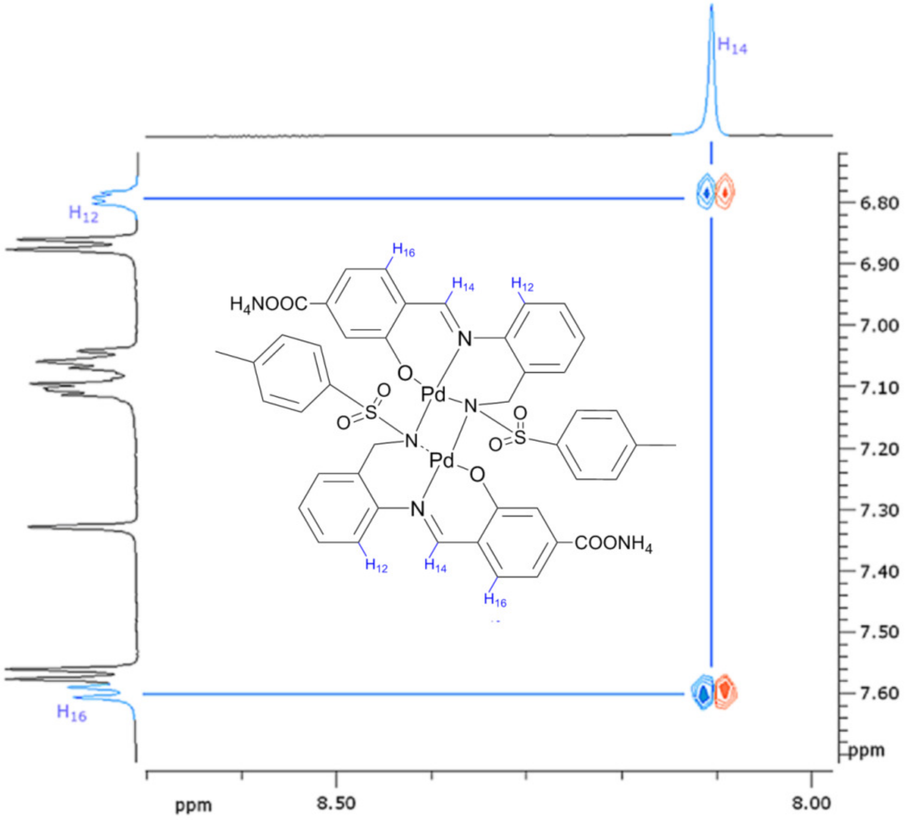


Fig.5. Partial view of the NOESY spectrum of $(NH_4)_2[Pd_2L_2]\cdot 2H_2O$ in DMSO-d_6

Conclusions

We have demonstrated that the ***N***-tosylated tridentate Schiff base ligand derived from the condensation of 2-tosylaminomethylaniline with 4-formyl-3-hydroxybenzoic acid (H_2L) is adequate to obtain dimeric complexes with some *d*-block metal ions. Further studies will be necessary to assay the catalytic activity the synthesised dinuclear complexes.

References

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