Different bridging preferences of zinc and palladium in dimeric complexes of a ligand based on 2-tosylaminomethylaniline

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Abstract: We report here the formation of dimeric palladium(II) and zinc(II) complexes of a ligand (H_2L) derived from the condensation of 2-tosylaminomethylaniline and 2,3-dihydroxybenzaldehyde. The structures in solution of the corresponding palladium(II) and zinc(II) complexes could be deduced from NMR studies. With the aim of establishing an energy-structure relationship between the two possible linkage isomers (μ-*O*-bridged and μ-*N*-bridged), some theoretical energy calculations have been performed.

Keywords

Linkage isomerism / Dimeric complexes, / Sulfonamido bridge / Phenoxo bridge

Introduction

Linkage isomerism attracts much interest, especially in connection to research on photochemical, biological and solid state reactions [1-3]. A bibliographic study on dinuclear complexes of N-tosylated tridentate ligands has shown that the two metals ions are typically bonded through μ_2-O_{phenoxo} [4,5] or μ_2-S_{mercapto} [6] bridges, but the structural characterisation of a dimeric copper complex displaying novel μ_2-$N_{\text{sulfonamido}}$ bridges [7] has demonstrated that this

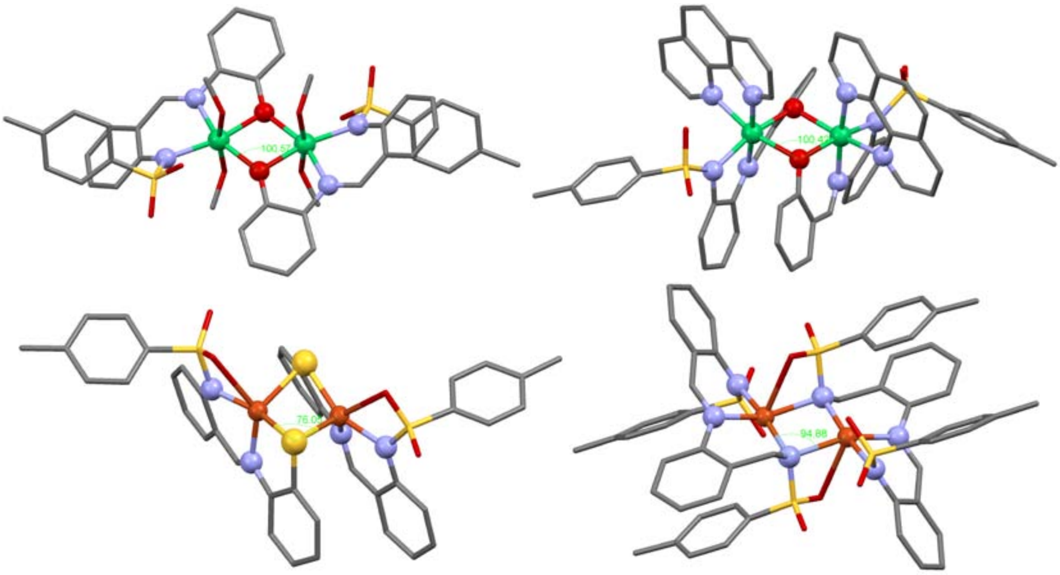

Fig. 1. Molecular structures of $Ni_2(L^a)_2(MeOH)_4\cdot 2MeCN$ (*top left*), $Ni_2(L^b)_2(phen)_2$(*top right.*), $Cu_2(L^c)_2$ (*top left*) and $Cu_2(L^d)_2$ (*top right*) showing the μ_2-O_{phenoxo} bridges (balls in red colour), μ_2-S_{mercapto} bridges (balls in yellow colour) and μ_2-$N_{\text{sulfonamido}}$ bridges (balls in blue colour).

unfamiliar bridge was also possible, as well as that N-tosylated tridentate Schiff base ligands could be versatile linkers. Fig. 1 shows the molecular structures of four dinuclear complexes displaying μ_2-O_{phenoxo}, μ_2-S_{mercapto} and μ_2-$\text{N}_{\text{sulfonamido}}$ bridges.

Since we have found that an *N,N,N*-donor Schiff base ligand based on 2-tosylaminomethylaniline was suitable for yielding dimeric Ni^{2+}, Pd^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} complexes through μ_2-$\text{N}_{\text{sulfonamido}}$ bridges [7], we have extended our investigations to H_2L, which is a tridentate linear ligand that can simultaneously bond two metals through either μ_2-O_{phenoxo} bridges or μ_2-$N_{\text{sulfonamido}}$ ones (Fig. 2). The easy bideprotonation of its OH and NH groups, as well as a suitable *N,N,O* binding domain have been considered during the design step of this N-tosylated tridentate Schiff base ligand, as adequate to forming dimeric complexes.

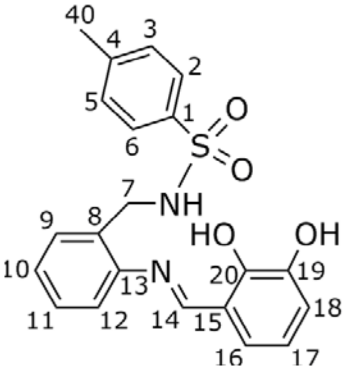

Fig. 2. Schematic representation of H_2L, showing the numbering scheme for NMR study.

Results and discussion

Synthesis of the compounds. H_2L has been synthesized in almost quantitative yield *via* nucleophilic addition of 2-tosylaminomethylaniline [8] to 2,3-dihydroxybenzaldehyde.

$Pd_2(L)_2$ could be prepared by reaction of $Pd(OAc)_2$ and H_2L in low yield, with formation of acetic acid during the reaction. In view of this fact, we have used an electrochemical method for the synthesis of $Zn_2(L)_2$, in which a zinc metal anode was oxidised in the presence of a solution of the ligand. This method is particularly adequate to forming complexes of the type M_2L_2 because during the process H_2 instead of H_3O^+ is evolved to the reaction medium, and therefore, bideprotonation of the ligand is not hindered.

Spectroscopic characterisation of the compounds. The structures of H_2L and its complexes were elucidated on the basis of NMR, FT-IR, and mass spectroscopies. The dinuclear nature of the zinc(II) and palladium(II) complexes is evidenced by the corresponding MALDI-TOF mass spectra. Single crystal X-ray diffraction techniques have provided precise information about the molecular structure of H_2L.

NMR assignment of the signals was made by a combination of COSY and NOESY experiments. The free Schiff base ligand was easily identified from the imino proton signal (8.7 ppm) and the magnetically equivalent methylene protons (4.1 ppm) [7]. The absence of the signals corresponding to the most acidic protons, *i.e.* those corresponding to the OH_{phenol} and $NH_{\text{sulphonamide}}$ groups, demonstrates the dianionic behavior of the ligand in $Zn_2(L)_2$ and $Pd_2(L)_2$.

The infrared spectra of H_2L displays five characteristic bands ring at about 3350, 3250, 1600, 1300 and 1150 cm^{-1}, which are attributed to ν(O–H), ν(N–H), ν(C=N), ν_{as}(S–O) and ν_s(S–O) vibrations, respectively. The absence of the two first bands in the spectra of the complexes supports the dianionic behaviour of the ligands after complexation.

Crystal structure of H_2L. Single crystal X-ray diffraction techniques have confirmed that orange prismatic crystals obtained after room temperature evaporation from a methanol solution of H_2L consist of crystallographically independent molecules of the enol tautomer of H_2L (Fig. 3). The enol nature of the molecule is deduced from the bond distances of the phenol groups. Bond distances and angles, which are shown in Table 1, fall within the usual ranges for related ligands [4-7].

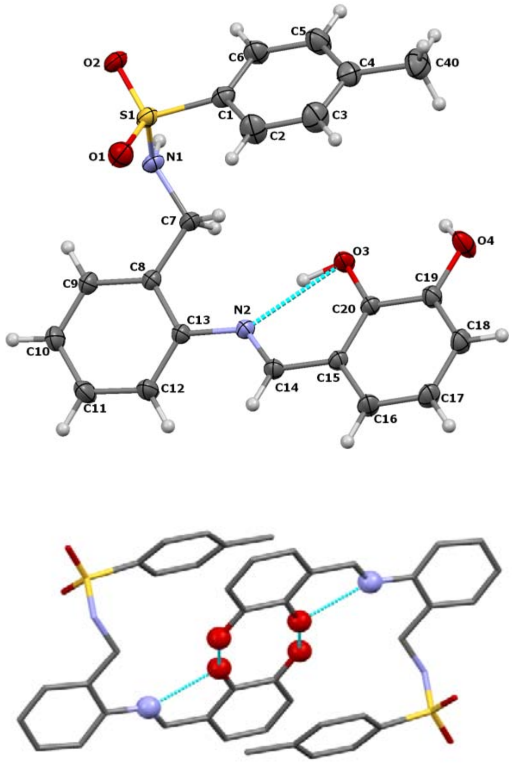

Fig. 3. *Top:* Ellipsoids view for the molecular structure of H_2L, showing an intramolecular H-bond. *Bottom*: Partial view of the crystal packing of H_2L showing intra- and intermolecular H-bonds that associate two contiguous molecules.

Table1. Main bond distances [Å] and angles [°] for H_2L.

Atoms	Distances	Atoms	Angles
C1-S1	1,760(2)	O1-S1-O2	120,12(9)
S1-O1	1,4279(15)	O1-S1-N1	106,86(10)
S1-O2	1,4355(14)	O2-S1-N1	105,98(9)
S1-N1	1,6181(19)	O1-S1-C1	107,85(10)
N1-C7	1,474(2)	N1-S1-C1	106,65(8)
C7-C8	1,506(2)	C7-N1-S1	116,99(13)
C12-C13	1,389(2)	N1-C7-C8	114,60(14)
C13-N2	1,421(2)	C12-C13-N2	122,14(15)
C14-N2	1,286(2)	C8-C13-N2	117,61(14)
C20-O3	1,3311(19)	N2-C14-C15	121,38(14)
C19-O4	1,353(2)	O3-C20-C15	122,23(15)
H-bonding		O3-C20-C19	118,65(14)
D-H···A	d(D-H)	O4-C19-C18	119,61(16)
N1-H1···O1$^{\#1}$	0,79(3)	C9-C8-C13	118,18(15)
O3-H3···N2	1,02(4)		
O4-H4···O3$^{\#2}$	0,81(4)		

$^{\#1}$ -x+2, -y-1, -z+1; $^{\#2}$ -x+2, -y, -z

The molecule of H_2L (Fig. 3) displays a typical *E* configuration, which is stabilized by the existence of the intramolecular H-bond O3-H3···N2 (Table 1) with one of the three potential donor atoms *exo* orientated in two separate binding sites, *N*,*O* and *N*. Intermolecular hydrogen bonds O3-H3···O4$^{\#}$, O4-H4···O3$^{\#}$ and N1-H···O$_{tosyl}$ in joint with other weaker interactions are responsible of the crystal packing.

Linkage isomerism study. The investigation was initiated to explore the presence of the O-bridged and N-bridged linkage isomers of $Zn_2(L)_2$ and $Pd_2(L)_2$ in solution using NMR spectroscopy.

Since the geminal protons at the methylene group (prochiral center) of $Zn_2(L)_2$ give rise to a single peak (isochronous NMR signal), they are enantiotopic protons (Fig. 4, left, δ = 3.90 ppm). This result is consistent with the idea that $Zn_2(L)_2$ exhibits rapid rotational motion of methylene groups on the NMR time scale at room temperature [9]. The two protons labelled as H7 can interconvert easily by fast rotation about a single carbon-carbon bond and therefore become equivalent. This spectral feature matches up with the observed in NMR spectra of free ligands based on 2-tosylaminomethylaniline and in its mononuclear complexes too [10]. A dimeric structure displaying μ_2-O_{phenoxo} bridges is consistent with a conformation that permits a rapid rotational motion of methylene groups on the NMR time scale [11].

In contrast, the ^{1}H NMR spectrum of $Pd_2(L)_2$ revealed two very different chemical shifts, 4.50 and 6.25 ppm (anisochronous NMR signal) for the two geminal protons of the methylene group (Fig. 4, right) despite being not placed in a chiral environment, and therefore are diastereotopic protons. The observed AB doublet with a chemical shift difference of *ca*. 1.75 ppm persists from -80 °C to the high-temperature limit of 40 °C in acetone-d_6. This result is consistent with the idea that $Pd_2(L)_2$ is conformationally locked and cannot undergo rapid rotational motion of methylene groups. A dimeric structure displaying μ_2-$N_{\mathrm{sulfonamido}}$ bridges is consistent with a conformation that prevents/hinders fast rotation about a single carbon-carbon bond on the NMR time scale.

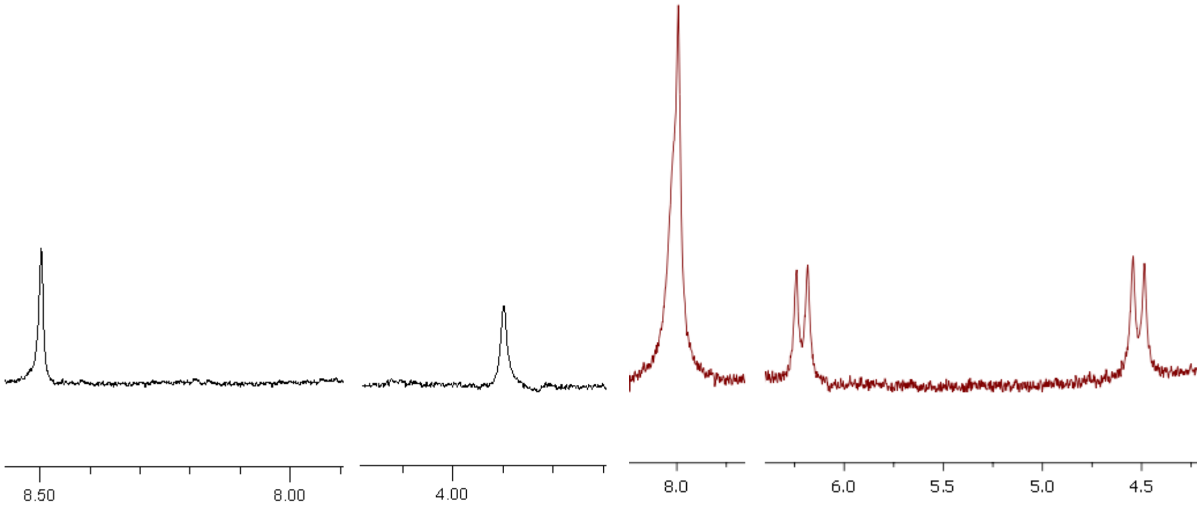

Fig.4 . Partial views of the ^{1}H NMR spectra of $Zn_2(L)_2$ (left) and $Pd_2(L)_2$ (right) in dmso-d_6 showing the most characteristic signals, *i.e.* imino and methylene protons signal.

To develop a structure–spectroscopic property relationship in dimeric complexes of the 2-tosylaminomethylaniline-based dianionic ligand L^{2-}, we explored the most stable conformations of the O-bridged and N-bridged linkage isomers of $Zn_2(L)_2$ and $Pd_2(L)_2$ using molecular mechanics modelling. We have considered both *syn* and *anti* conformations of each μ_2-O and μ_2-N isomer, meaning that the two tosyl groups of the complexes are positioned at the same side or at opposite sides of central metallacycles (M_2B_2, where M = Zn, Pd and B = O, N) respectively. Results have revealed that the most stable linkage isomer of $Zn_2(L)_2$ is the form *syn*-μ_2-O (Fig. 5, bottom), while the form *syn*-μ_2-N (fig. 5, top) is the most stable isomer of $Pd_2(L)_2$. The observed NOESY cross-peaks, showing both the *E* configuration of L^{2-} and the close proximity of the benzylidene ring to the tosyl ring, support the predicted most stable conformations of *syn*-μ_2-N-$Pd_2(L)_2$ and *syn*-μ_2-O-$Zn_2(L)_2$.

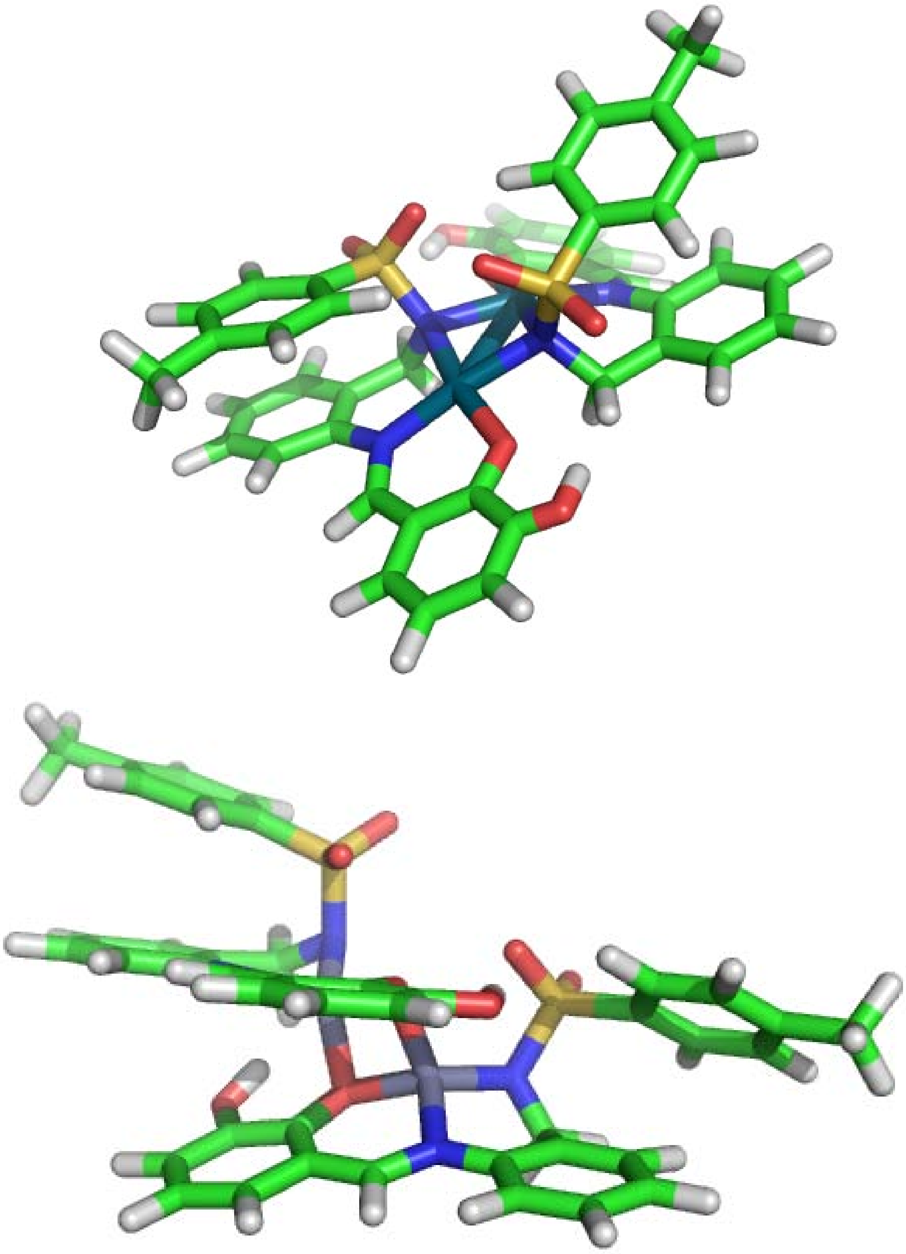

Fig. 5. Minimum energy conformations of isomers *syn*-μ_2-N-$Pd_2(L)_2$ (top) and *syn*-μ_2-O-$Zn_2(L)_2$ (bottom)

Conclusions

We have demonstrated that N-tosylated tridentate Schiff base ligand H_2L derived from the condensation of 2-tosylaminomethylaniline and 2,3-dihydroxybenzaldehyde is adequate to obtain linkage isomers O-bridged and N-bridged. Experimental studies in solution have revealed the formation of *syn*-μ_2-O-$Zn_2(L)_2$ and *syn*-μ_2-N-$Pd_2(L)_2$. Theoretical calculations support the latter.

Experimental

Syntheses of the ligand

H_2L: A solution (absolute ethanol, 40 mL) of 2,3-dihydroxybenzaldehide (0,15 g, 0,73 mmol) and 2-tosylaminomethylaniline (0,20 g, 0,73 mmol) in was heated under reflux for 3 h. The resulting orange solution was concentrated to dryness under vacuum resulting in an oily fluid, which after stirring with diethyl ether (20 mL) for 8h leads to an orange solid that was filtered off and then dried under vacuum. Recrystallization of the brute in methanol leads to prismatic orange crystals, which were adequate to single X-ray diffraction techniques. Yield = 0,22 g (76%). Mp = 141 °C. ^1H NMR (500 MHz, DMSO-d_6, δ in ppm): 12,56 (s, 1H, HO20), 9,28 (s, 1H, HO19), 8,70 (s, 1H, H14), 8,06 (t, J = 5,9 Hz, 1H, HN), 7,64 (d, J = 8,5 Hz, 2H, H2 + H6), 7,36 (d, 1H, H16; t, 1H, H17), 7,30 (d, 2H, H3 + H5; d, 1H H18), 7,23 (t, J = 7,7 and 1,4 Hz, 1H, H10), 7,10 (d, J = 7,7 and 1,4 Hz, 1H, H12), 6,96 (d, J = 7,7 and 1,4 Hz, 1H, H9), 6,79 (t, J = 7,7 Hz, 1H, H11), 4,10 (d, J = 5,3 Hz, 2H, H7), 2,34 (s, 3H, H40). IR (KBr, ν/cm^{-1}): ν(OH) 3414, ν(NH) 3293, $\nu(C{=}N_{imi})$ 1619, $\nu_{as}(SO_2)$ 1329, $\nu_s(SO_2)$ 1158. MS (ESI$^+$, MeOH/HCOOH) *m/z* (%) [adduct]: 419,2 (50) $[H_2L+Na]^+$. Elemental analyses: C 63,8; H 5,3; N 7,0; S 8,1%; calc for $C_{21}H_{20}N_2O_4S$: C 63,6; H 5,1; N 7,1; S 8,1%

Crystal data for H_2L: triclinic, *P*-1, $C_{21}H_{20}N_2O_4S$, *Mw* = 396.45, a = 8.979(5) Å, b = 10.358(5) Å , c = 12.109(5) Å, α = 68.918(5) °, β = 67.153(5) °, γ =88.425(5) °; V = 960.1(8) Å^3, Z = 3; ρ_{calc} = 1.371 g.cm^{-3}; R_1 = 0.0461 and $wR2$ = 0.1399 ($I > 2\sigma I$), R_1 = 0.0596 and wR_2 = 0.3020 (all data), residual electron density 0.403 and -0.297 e.Å^3.

Syntheses of the complexes

$Zn_2(L)_2$: The zinc complex has been obtained by an electrochemical method, in which a sacrificial metal anode was oxidised in an acetonitrile solution of H_2L leading to $Zn^{2+}_{(MeCN)}$ + $L^{2-}_{(MeCN)}$ + H_2. The cell can be summarized as: Zn(+)|$H_2L_{(MeCN)}$ + $NEt_4ClO_{4(MeCN)}$|Pt(–). ***(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!).* An acetonitrile solution (80 mL) of H_2L (0,05 g, 0,13 mmol), containing tetraethylammonium perchlorate (ca. 50 mg) that is used as supporting electrolyte, was electrolysed for 1h and 21 min at a current intensity of 5.2 mA and an initial voltaje of 5 V. The resulting pale yellow precipitate was filtered off, washed with acetonitrile (20 mL) and then dried under vacuum. Yield: 0,05 g (96%). ^{1}H NMR (250 MHz, DMSO-d_6, δ en ppm): 9,15 (s, 1H, HO19), 8,50 (s, 1H, H14), 7,67 (d, J = 8,1 Hz, 2H, H2 + H6), 7,34 (d, 1H, H16; t, 1H, H17), 7,21 (d, 2H, H3 + H5), 7,17 (t, J = 7,7 Hz, 1H, H10), 7,14 (t, J = 7,7 Hz, 1H, H11), 7.04 (d, J = 7,1 Hz, 1H, H18), 6,90 (d, J = 8.1 Hz, 1H, H12), 6,84 (d, J = 7.5 Hz, 1H, H9), 3.94 (s, 2H, H7), 2,31 (s, 3H, H40). MS (ESI$^+$, MeOH/HCOOH) m/z (%) [adduct]: 921.2 (12), $[Zn_2(L)_2+H]^+$; 460.2 (100), $[Zn(L)+H]^+$. IR (KBr, ν/cm^{-1}): ν(OH) 3415, ν(C=N) 1595, $\nu_{as}(SO_2)$ 1264, $\nu_s(SO_2)$ 1158. Elemental analysis: C 54.5; H 4.4; N 6.2; S 7.2%, calc. for $C_{42}H_{36}N_4O_8S_2Zn_2$: C 54.9; H 4.0; N 6.1; S 7.0%.

$Pd_2(L)_2$: A solution (methanol, 40 mL) of H_2L (0,05 g, 0,13 mmol) and $Pd(OAc)_2$ (0,03 g, 0,13 mmol) was stirred at room temperature for 4h and 30min. The resulting orange precipitate was filtered off, washed with methanol and then dried under vacuum. Yield = 0,03 g (55%). ^{1}H NMR (250 MHz, DMSO-d_6, δ en ppm): 8,04 (s, 2H, HO19), 8,01 (s, 2H, H14), 7,26 (m, 8H, H2+H6, H16, H17), 7,11 (d, J = 8,5 Hz, 2H, H18), 6,98 (m, 6H, H3 + H5, H10), 6, 89 (d, J = 7,0 Hz, 2H, H12), 6,84 (d, J = 7,8 Hz, 2H, H9), 6,57 (t, J = 7,7 Hz, 2H, H11), 6,23 (d, J = 14,2 Hz, 2H, H7), 4,53 (d, J = 14,2 Hz, 2H, H7), 2,26 (s, 6H, H40). IR (KBr, ν/cm^{-1}): ν(OH) 3429, ν(C=N$_{\text{imi}}$) 1618, $\nu_{as}(SO_2)$ 1333, $\nu_s(SO_2)$ 1151. MS (MALDI-TOF$^+$, DCTB) m/z (%) [adduct]: 1002,0 (9) $[Pd_2(L)_2+H]^+$, 501,2 (100) $[Pd(L)+H]^+$. Elemental analyses: C 50,7; H 3,7; N 5,9; S 6,6%; calc. for $C_{42}H_{36}N_4O_8Pd_2S_2$: C 50,4; H 3,6; N 5,6; S 6,4%.

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