Synthesis, Characterisation, and X-ray Crystal Structure of New Ni^{II}, Pd^{II}, and Pt^{II} Complexes of Tridentate Pyrazole-Based Ligands with an NOS-Donor Set

Jordi García-Antón,[a] Josefina Pons,*[a] Xavier Solans,[b] Mercè Font-Bardia,[b] and Josep Ros*[a]

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Treatment of the ligands 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd) and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd) with $[PdCl_2(CH_3CN)_2]$, $[PtCl_2(CH_3CN)_2]$, and $NiCl_2{\cdot}6H_2O$ produces the complexes $[MCl_2(L)]$ [M= Pd, L = thpd (**1**), thhd (**2**); M = Pt, L = thpd (**3**), thhd (**4**); M = Ni, L = thpd (**5**), thhd (**6**)], which have been characterised by elemental analyses, conductivity, IR, electronic spectra, and NMR spectroscopy (when possible). The crystal structures of **2**, **3**, and **4**, determined by single-crystal X-ray diffraction, each consist of discrete $[MCl_2(L)]$ units. Each M^{II} atom is coordinated by the pyrazolyl nitrogen and the thioether sulfur from the ligand and two *cis* chloride ions in a square-planar geometry. Crystallisation of $[NiCl_2(thpd)]$ in non-anhydrous alcohols yields $[NiCl(H_2O)_2(thpd)]Cl$ ([**7**]Cl), the crystal structure of which was determined by single-crystal X-ray diffraction to reveal nickel atoms coordinated by two water molecules, one chloride ion and one thpd ligand (coordinating via all three donor atoms, N, S, and O) in a skew-trapezoidal bypyramid (distorted octahedral) geometry.
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Introduction

The coordination chemistry of chelating ligands containing mixed functionalities is of continued importance.[1] In particular, the chemistry of ligands that contain both inert and labile groups has received considerable attention.[2] Jeffrey and Rauchfuss first introduced the term "hemilabile ligand" in 1979[3] to describe polydentate chelates that contain at least two different types of bonding groups — a hard and a soft donor group[4] — making them attractive for catalytic purposes.

Our group has previously synthesised and characterised pyrazolic ligands with two donor groups, in particular N−N(amine),[5] N−P,[6] N−O,[7] and N−S.[8] Our next goal is to study the coordinative properties of ligands with three donor groups.

Here, we report the synthesis and full characterisation of two new ligands, 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd), and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd), the three different donor atoms in this case being nitrogen, sulfur, and oxygen. The complexation of these ligands with $[MCl_2(CH_3CN)_2]$ (M = Pd^{II}, Pt^{II}) and $NiCl_2{\cdot}6H_2O$ is also reported, to give the complexes: $[MCl_2(L)]$ [M= Pd, L = thpd (**1**), thhd (**2**); M = Pt, L = thpd (**3**), thhd (**4**); M = Ni, L = thpd (**5**), thhd (**6**)]. Treatment of **5** with non-anhydrous alcohols produces $[NiCl(H_2O)_2(thpd)]Cl$ ([**7**]Cl). These complexes have been characterised by elemental analyses, conductivity, IR spectroscopy and, when possible, ^1H NMR, $^{13}C\{^1H\}$ NMR, and $^{195}Pt\{^1H\}$ NMR spectroscopy. The X-ray crystal structures of complexes **2**, **3**, **4**, and [**7**]Cl are also presented.

Results and Discussion

The ligands 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd) and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd), not previously reported, were synthesised to initiate a new study of pyrazole-based ligands with N1 alkyl substituents containing two different donor atoms (in this case O and S). In this respect, 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl 4-methylbenzenesulfonate[9] on treatment with 2-mercaptoethanol gave thpd and 1-(2-mercaptoethyl)-3,5-dimethylpyrazole[10] on treatment with 3-chloro-1-propanol gave thhd (Scheme 1). These ligands were characterised by elemental analysis, MS spectrometry, and infrared, ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopy.

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[a] Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona,
08193 Bellaterra-Cerdanyola, Barcelona, Spain
Fax: (internat.) + 34-93/581-3101
E-mail: Josefina.Pons@uab.es
[b] Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona,
Martí i Franquès s/n, 08028 Barcelona, Spain

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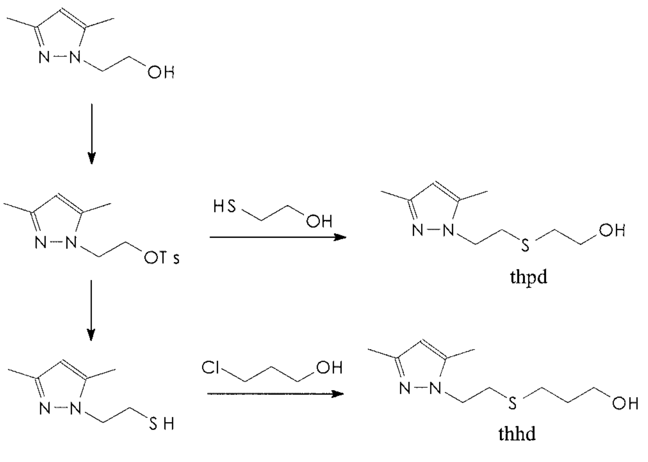

Scheme 1

Treatment of thpd and thhd with $[MCl_2(CH_3CN)_2]$ (M = Pd^{II} [11] and Pt^{II} [12]) produced four chloro complexes whose elemental analyses agree with the formula $[MCl_2(L)]$ [M = Pd, L = thpd (**1**), L = thhd (**2**); M = Pt, L = thpd (**3**), L = thhd (**4**)]. Conductivity values in acetonitrile for complexes **1−4** reveal a non-electrolyte nature [1.8−6.4 $\Omega^{-1}cm^2mol^{-1}$]. The reported values for 10^{-3} M solutions of non-electrolyte complexes are lower than 120 $\Omega^{-1}cm^2mol^{-1}$ in acetonitrile.[13]

The IR spectra of the complexes **1−4** are similar to those of the ligands, the most characteristic bands being those attributable to the pyrazolyl group, ν(C = C) and ν(C = N) between 1553 and 1548 cm^{-1} and $\delta(C-H)_{oop}$ between 828 and 785 cm^{-1}.[14]

Suitable single crystals for X-ray structure determination were obtained by recrystallisation from methanol for **2−4**.

^1H and ^{13}C NMR spectra of **1−4**, recorded in [D$_3$]acetonitrile, show the signals of the coordinated ligands (data are reported in the Exp. Sect.). HMQC spectra at 253 K were used to assign the proton signals (e.g. for **3** in Figure 1).

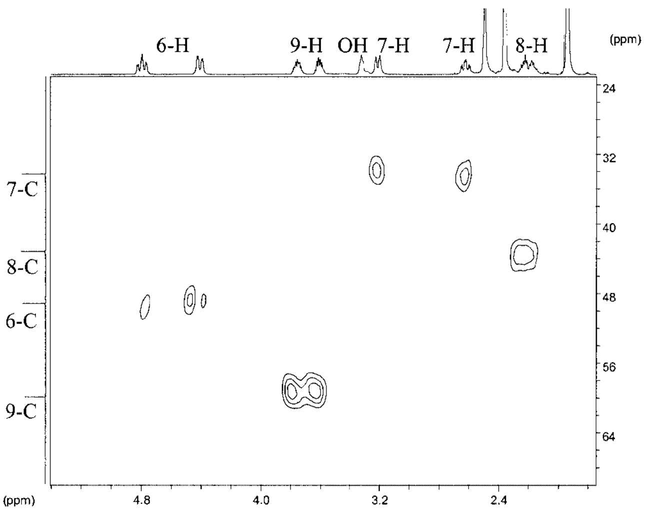

Figure 1. 250 MHz 2D HMQC spectrum of **3** at 253 K

The ^1H NMR spectra of complexes **1−4** at 298 K show sharp resonances for the CH and CH_3 groups of the pyrazolyl cycles. For **1** and **2**, only one broad band can be attributed to each CH_2 in the $S-(CH_2)_2-N$ and $S-(CH_2)_x-OH$ (x = 2 for **1** and x = 3 for **2**) chains, whereas at 253 K, the two protons of each CH_2 (in both chains) can be assigned to two different signals (although some of the signals are partially superposed and are given as a single multiplet in the Exp. Sect.). These two signals for each CH_2 are due to the rigidity of these chains, at 253 K, giving rise to two diastereotopic hydrogens for each CH_2.

At 298 K, for complexes **3** and **4**, two broad bands can be assigned to each CH_2 in the $S-(CH_2)_2-N$ chain but only one signal for each CH_2 in the $S-(CH_2)_x-OH$ (x = 2 for **3** and x = 3 for **4**) chain. At 253 K, signals attributable to the CH_2 in the $S-(CH_2)_2-N$ chain become well-defined multiplets and the CH_2 corresponding to the $S-(CH_2)_x-OH$ chain show two well-defined signals for each of them (but, as for the Pd^{II} complexes, some of these signals are superposed and are given as a single multiplet in the Exp. Sect.).

The broad bands for **1−4** at 298 K arise from fluxional processes that involve the $S-(CH_2)_2-N$ and $S-(CH_2)_x-OH$ (x = 2 for **1**, **3** and x = 3 for **2**, **4**) chains. This led us to record variable-temperature spectra for **1−4** (spectra for 6-H, 9-H and the alcohol group for **3** are shown in Figure 2). The two different chains [$S-(CH_2)_2-N$ and $S-(CH_2)_x-OH$] were studied separately.

For the $S-(CH_2)_2-N$ chain, the two CH_2 signals coalescence to one at 273 and 293 K for complexes **1** and **2**, respectively, whereas **3** and **4** required heating to 338 and 345 K, respectively, to bring about coalescence. These temperature coalescences and the separation of the two signals attributed to each CH_2 correspond to $\Delta G^{\ddagger}$ values of ca. 55, 59, 66, and 68 kJ·mol^{-1} for **1−4**, respectively.[15]

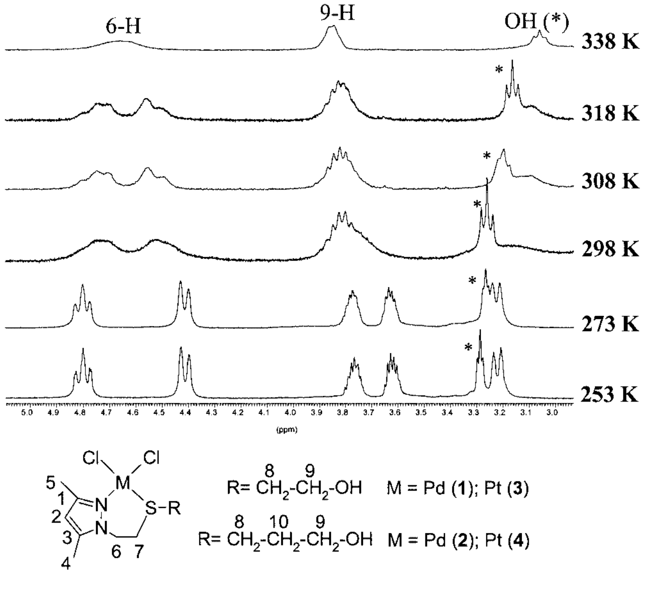

Figure 2. Numbering scheme for the complexes **1−4** and ^1H NMR variable-temperature experiments for 6-H and 9-H in **3**

The $\Delta G^{\ddagger}$s are consistent with a chelate ring-flipping process due to the rocking of the pyrazolyl cycle around the M−N bond without any metal−ligand bond breaking.[5e,7c] At higher temperatures, with ring-flipping, the two hydrogens of each CH_2 are interconverted and only one signal can be observed. These energy values could also be consistent with a mechanism that implies an inversion of the sulfur atom configuration.[16,17]

For the $S-(CH_2)_x-OH$ chains ($x = 2$ for **1** and **3** and $x = 3$ for **2** and **4**) the rigidity could be attributed to hydrogen bonds that occur only at low temperatures. This would explain why the hydrogens of these chains appear as diastereotopic at 253 K. Definitive evidence for O−H···Cl interactions in the solid state is given by the X-ray analyses of **2**−**4**. The existence of these interactions in solution was proved by the variable-temperature spectra of the alcohol group (example for **3** in Figure 2) in which the chemical shift of the alcohol group varied with temperature (from $\delta = 3.23$ and 2.78 ppm at 298 K to $\delta = 3.36$ and 3.03 ppm for **1** and **2**, respectively and from $\delta = 3.06$ and 2.83 ppm at 338 K to $\delta = 3.29$ and 3.09 at 253 K for **3** and **4**, respectively). The R−OH resonances shift to lower fields with decreasing temperature, as expected for this kind of process.[18]

For the $S-(CH_2)_x-OH$ chains the two CH_2 signals coalescence at 298 K for complexes **1**−**4**, which, together with the separations of the two signals, corresponds to $\Delta G^{\ddagger}$s of ca. 61 kJ·mol^{-1} for **1** and **3** and ca. 63 and 66 kJ·mol^{-1} for **2** and **4**, respectively.[15]

Additional $^{195}Pt\{^{1}H\}$ NMR experiments for complexes **3** and **4** at 298 K revealed only one band for each complex ($\delta = -2868$ ppm for **3** and -2879 ppm for **4**). This suggests that all of the bands in the ^{1}H NMR spectra belong to only one complex, as expected from the data obtained with the variable-temperature experiments.

Treatment with $NiCl_2·6H_2O$ led to the isolation of one complex for each ligand. Their elemental analyses agree with the formula $[NiCl_2(L)]$ [L = thpd (**5**) and thhd (**6**)]. The molar conductivities in absolute ethanol are consistent with non-electrolyte complexes [14.3−18.7 $\Omega^{-1}cm^{2}mol^{-1}$]. Reported values for 10^{-3} M solutions of non-electrolyte complexes in absolute ethanol are lower than 35 Ω^{-1} cm^{2} mol^{-1}.[13] The IR spectra (4000−400 cm^{-1}) of complexes **5** and **6** are similar to those of the ligands.[14] Additional spectra in the region 500−100 cm^{-1} present well-defined bands corresponding to ν(Ni−N) (450, 461 cm^{-1}), ν(Ni−Cl) (368, 387 cm^{-1}), and ν(Ni−S) (328, 344 cm^{-1}) bands for **5** and **6**, respectively, and a band attributable to ν(Ni−O) at 498 cm^{-1} for **5** and 520 cm^{-1} for **6**.[19]

Electronic spectra of the complexes **5** and **6** measured in absolute ethanol show a single d-d band at 422 nm ($\varepsilon = 55$ mol^{-1}cm^{-1}L) for **5** and 414 nm ($\varepsilon = 75$ mol^{-1}cm^{-1}L) for **6** that can be attributed to the $^{3}E'(F)\rightarrow{}^{3}E''(P)$ transition, which is characteristic for pentacoordinate Ni^{II} complexes.[20] It was not possible to obtain single crystals of these complexes.

When **5** was dissolved in methanol or ethanol it reacted with the water in the solvent to give a complex that was obtained as suitable single crystals for X-ray structure determination. This complex {$[NiCl(H_2O)_2(thpd)]Cl$ ([**7**]Cl)} has an IR spectrum with bands that can be attributed to water molecules not observed for complex **5**. The electronic spectrum of complex [**7**]Cl was measured in ethanol and shows two bands in the visible region at 731 ($\varepsilon = 4$ mol^{-1}cm^{-1}L) and 403 nm ($\varepsilon = 10$ mol^{-1}cm^{-1}L), which can be attributed to $^{3}A_{2g}\rightarrow{}^{3}T_{1g}(F)$ and $^{3}A_{2g}\rightarrow{}^{3}T_{1g}(P)$ transitions, respectively, these being characteristic for octahedral Ni^{II} complexes.[20] An equivalent complex with thhd could not be isolated.

Crystal Structure of $[MCl_2(L)]$ [M= Pd, L = thhd (2); M = Pt, L = thpd (3), thhd (4)]

The structure of **2** consists of discrete $[PdCl_2(thhd)]$ units (Figure 3), while **3** and **4** consist of discrete $[PtCl_2(L)]$ (L = thpd and thhd, respectively) units (Figures 4 and 5, respectively). Crystallographic data for complexes **2** and **4** indicate that they are isostructural.

The metal atom of each structure is surrounded by an identical *core* composed of the nitrogen and thioether sulfur from the pyrazole ligand and two chlorine atoms. The metal atoms have a slightly distorted square-planar geometry, with the chloride ions in a *cis* arrangement. A small tetrahedral distortion can be observed in the mean separation of the atoms linked to the metal cation in relation to the mean plane [±0.065(4) Å for **2**, ±0.001(3) Å for **3**, and ±0.050(3) Å for **4**].

Some selected bond lengths and bond angles are listed in Table 1. There are two complexes in the literature with a $PdCl_2NS$ *core* (terminal chloride ion, pyrazolic nitrogen, and tioether sulfur). For complex **2**, Pd−Cl, Pd−N, and

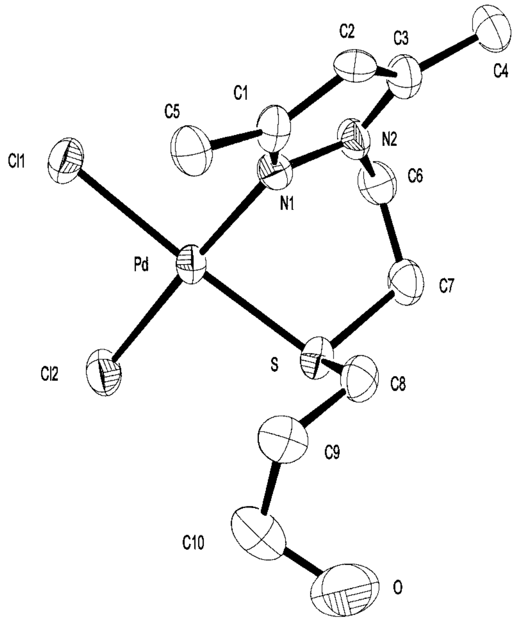

Figure 3. ORTEP drawing of $[PdCl_2(thhd)]$ (**2**, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

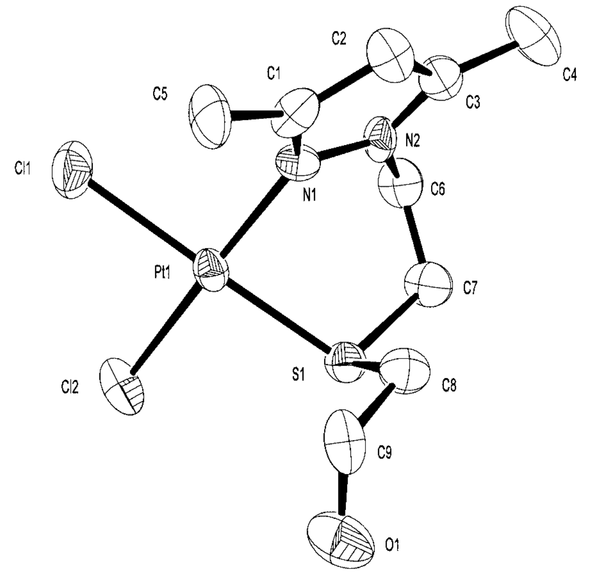

Figure 4. ORTEP drawing of $[PtCl_2(thpd)]$ (**3**, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

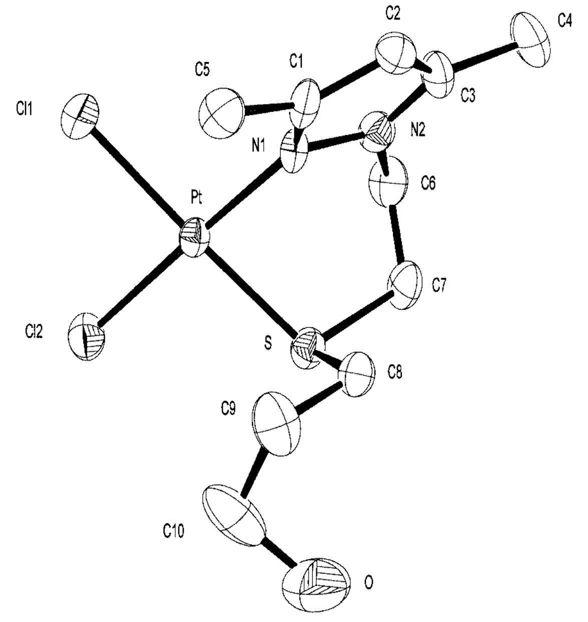

Figure 5. ORTEP drawing of $[PtCl_2(thhd)]$ (**4**, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

Pd−S bond lengths are similar to those found for the two reported complexes.[21]

No structural data for complexes with a $PtCl_2NS$ *core* (terminal chloride ion, pyrazolic nitrogen, and thioether sulfur) have been reported, although two structures with a $PtCl_2NS$ *core* (aromatic amine) have been described[22] in addition to five complexes with a PtN_2Cl_2 *core* (terminal chloride and pyrazolic nitrogen) have been described.[23] For complexes **3** and **4**, the Pt−S,[22] Pt−N,[23] and Pt−Cl[24] bond lengths are of the same order as those found in the literature.

The thpd and thhd ligands act as bidentate chelates, and form one M−S−C−C−N−N six-membered ring in each complex, all of which have a boat conformation. Bite angles are 86.9(1)° for N(1)−Pd−S in **2** and 87.7(1)° and 87.5(3)° for N(1)−Pt−S in **3** and **4**, respectively. For complex **2** this bite angle is similar to those reported for $[Pd(bddo)](BF_4)_2{\cdot}H_2O$ [bddo = 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane], 88.8(2) and 86.2(1)°,[8a] and $[Pd(pdto)](ClO_4)_2$ [pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane], 86.9° and 87.2°.[25]

Distortion of the boat conformation in six-membered rings is observed in ΔC_s [for, **2** $\Delta C_s(Pd)$ = 6.8(4)° and $\Delta C_s(S-C7)$ = 11.0(5)°; for **3** $\Delta C_s(Pt)$ = 16.0(9)° and $\Delta C_s(S-C7)$ = 16.3(10)°; and for **4** $\Delta C_s(Pt)$ = 6.1(3)° and $\Delta C_s(S-C7)$ = 13.7(4)°; $\Phi_i+\Phi_i'$= torsion angles related to the considered plane;[26] m = equivalent torsion angles].

$$\Delta C_S = \sqrt{\frac{\sum_{i=1}^{m}(\phi_i + \phi_i')^2}{m}}$$

Complexes **2**−**4** contain intermolecular hydrogen bonds between Cl and OH (Table 2). Complexes **2** and **4** yield infinite chains parallel to the crystallographic vector *b*, whereas the chains for complex **3** are parallel to the crystallographic vector *c* (an example for **4** is given in Figure 6).

Crystal Structure of $[NiCl(H_2O)_2(thpd)]Cl$ ([7]Cl)

The structure of [**7**]Cl consists of cationic units of $[NiCl(H_2O)_2(thpd)]^+$ and chloride anions (Figure 7). The ligand is coordinated to the metallic centre by the nitrogen, sulfur, and oxygen atoms. Nickel(II) completes its coordination with one chloride ion and two water molecules in a skew-trapezoidal bipyramid (distorted octahedral) geometry (Cl1, N1, O2, O3, and Ni atoms being in a plane) with angles at Ni^{II} in the range 83.68(8)−96.90(9)° and 168.32(6)−176.16(7)°. Water molecules are arranged *trans* to the sulfur and the nitrogen atoms, and the chloride ion is *trans* to the alcohol group.

Some selected bond lengths and bond angles are listed on Table 3. No other complex with a $NiClNO_3S$ *core* appears in the literature. The Ni−O, $Ni-OH_2$, Ni−S, Ni−Cl, and Ni−N bond lengths are of the same order as those found for Ni−O(alcohol),[27] $Ni-OH_2$ (complexes containing two water molecules),[28] Ni−S(thioether),[9,27a,29] Ni−Cl(terminal),[27b,28d,29b,29d,30] and Ni−N(pyrazole)[9,27−30] bond lengths, respectively.

The thpd ligand acts as a tridentate chelate and forms one Ni−S−C−C−O five-membered ring with an envelope conformation [C9 being ±0.457(4) Å out of the plane formed by the other four atoms] and one Ni−N−N−C−C−S six-membered ring with a boat conformation. Distortion of the boat in the six-membered ring is observed in $\Delta C_s(Ni)$ = 13.2(2)° and $\Delta C_s(S-C7)$ = 55.9(2)°.

Table 1. Selected bond lengths (Å) and angles (°) for **2**−**4** with estimated standard deviations (e.s.d.s.) in parentheses

2		**3**		**4**	
Pd−N(1)	2.001(5)	Pt−N(1)	2.024(8)	Pt−N(1)	2.002(3)
Pd−S	2.279(2)	Pt−S	2.260(3)	Pt−S	2.2588(10)
Pd−Cl(2)	2.280(2)	Pt−Cl(2)	2.311(3)	Pt−Cl(2)	2.2909(11)
Pd−Cl(1)	2.326(2)	Pt−Cl(1)	2.321(4)	Pt−Cl(1)	2.3263(10)
N(1)−Pd−S	86.91(14)	N(1)−Pt−S	87.5(3)	N(1)−Pt−S	87.72(10)
N(1)−Pd−Cl(2)	176.03(13)	N(1)−Pt−Cl(2)	177.1(2)	N(1)−Pt−Cl(2)	177.69(10)
S−Pd−Cl(2)	90.49(6)	S−Pt−Cl(2)	90.73(16)	S−Pt−Cl(2)	90.84(4)
N(1)−Pd−Cl(1)	91.58(13)	N(1)−Pt−Cl(1)	91.7(3)	N(1)−Pt−Cl(1)	91.18(10)
S−Pd−Cl(1)	175.91(5)	S−Pt−Cl(1)	177.46(11)	S−Pt−Cl(1)	176.41(4)
Cl(1)−Pd−Cl(2)	91.21(6)	Cl(1)−Pt−Cl(2)	89.98(14)	Cl(1)−Pt−Cl(2)	90.37(4)

Table 2. Distances and angles related to hydrogen bonding

Compound	D−H	H···A	D···A	D−H···A
2				
O−H(10)···Cl(1)	0.82(8)	2.43(8)	3.235(8)	165(4)
3				
O−H(10)···Cl(2)	0.82(9)	2.40(9)	3.214(12)	174(6)
4				
O−H(10)···Cl(1)	0.82(4)	2.44(4)	3.235(5)	164(2)
[**7**]Cl				
O(1)−H(10)···Cl(2)	0.78(3)	2.44(3)	3.110(4)	145(2)
O(2)−H(20)···Cl(2)	0.78(2)	2.42(2)	3.148(4)	157(3)
O(3)−H(30)···Cl(2)	0.66(4)	2.42(4)	3.077(4)	173(4)

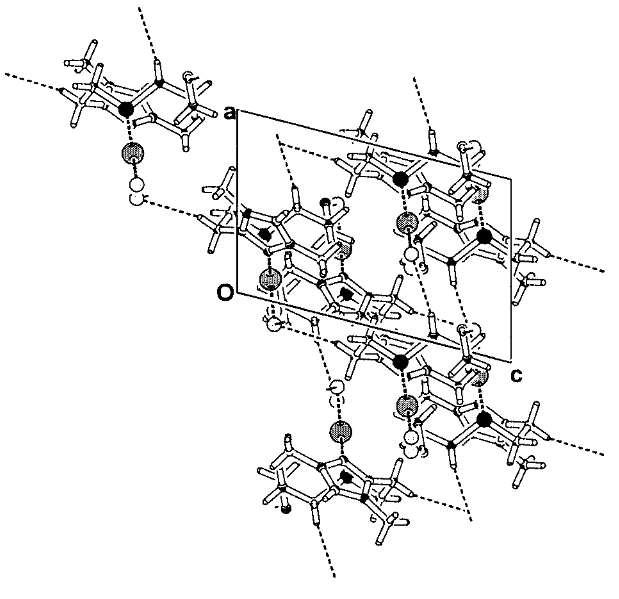

Figure 6. Partial view of the infinite chain formed by the different units of $[PtCl_2(thhd)]$ (**4**) bonded by hydrogen bonds

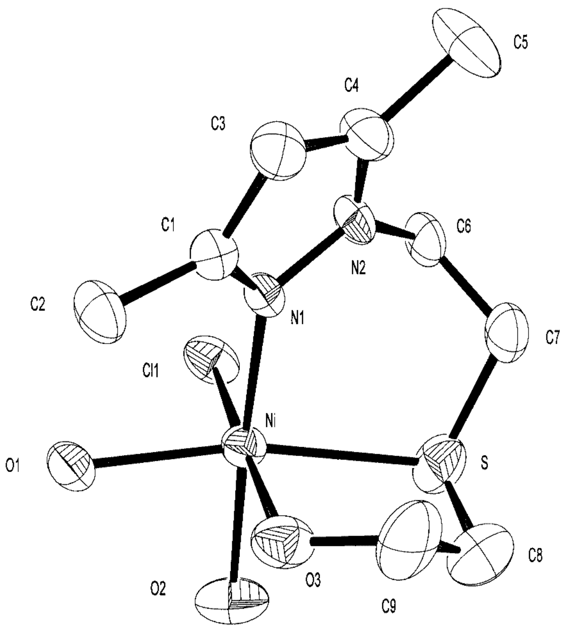

Figure 7. ORTEP drawing of $[NiCl(H_2O)_2(thpd)]^+$ ($[\mathbf{7}]^+$, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

For the six-membered ring, the N(1)−Ni−S bite angle is 93.12(8), while for the five-membered ring the S−Ni−O(3) bite angle is 83.68(8)°. The N−Ni−S bite angle is greater and the S−Ni−O is similar to those reported in the literature for $[Ni_3(bdnol)Cl_5(EtOH)]\cdot 3EtOH$ (N−Ni−S bite angles are 89.991° and 91.634° and S−Ni−O bite angles are 82.177° and 84.090°) and $[Ni_2(bdnol)Cl_3]\cdot MeCN$ [bdnol = 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol] (N−Ni−S bite angles are 91.514°and 91.755° and S−Ni−O bite angles are 83.952° and 84.016°).[29b]

This complex contains three types of hydrogen bonds, intramolecular O(1)−H(10)···Cl(2) and intermolecular O(2)−H(20)···Cl(2) and O(3)−H(30)···Cl(2). The O(2)−H(20)···Cl(2) bonding yields a four-membered circuit and O(3)−H(30)···Cl(2) furnishes infinite chains parallel to the crystallographic vector *a* (Table 2, Figure 8).

Conclusion

The structures of the chlorocomplexes presented here were originally investigated to discover the configuration of the new potentially tridentate N, O, S ligands 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd) and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd) when com-

Table 3. Selected bond lengths (Å) and angles (°) for $[\mathbf{7}]^+$ with estimated standard deviations (e.s.d.s.) in parentheses

	$[\mathbf{7}]^+$
Ni−O(1)	2.060(3)
Ni−N(1)	2.082(2)
Ni−O(2)	2.121(2)
Ni−O(3)	2.114(2)
Ni−Cl(1)	2.3881(12)
Ni−S	2.408(2)
O(1)−Ni−N(1)	96.90(9)
O(1)−Ni−O(3)	90.38(10)
N(1)−Ni−O(3)	86.83(9)
O(1)−Ni−O(2)	84.46(11)
N(1)−Ni−O(2)	172.78(9)
O(3)−Ni−O(2)	86.03(9)
O(1)−Ni−Cl(1)	91.58(8)
N(1)−Ni−Cl(1)	96.22(7)
O(3)−Ni−Cl(1)	176.16(7)
O(2)−Ni−Cl(1)	90.88(7)
O(1)−Ni−S	168.32(6)
N(1)−Ni−S	93.12(8)
O(3)−Ni−S	83.68(8)
O(2)−Ni−S	85.10(9)
Cl(1)−Ni−S	93.81(6)

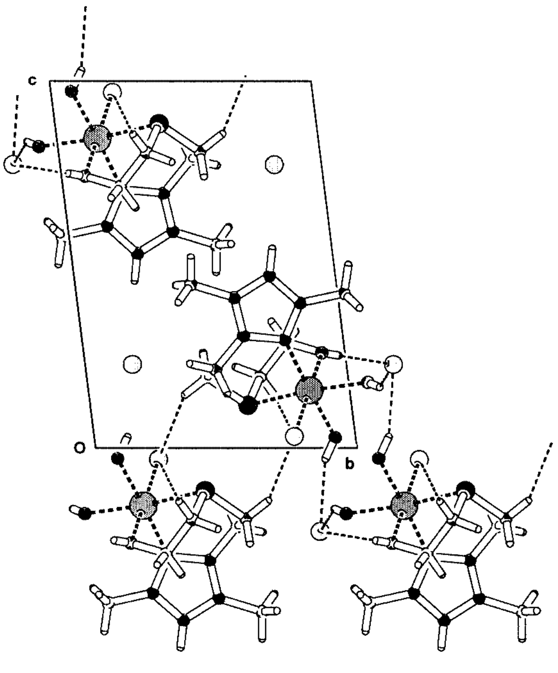

Figure 8. Partial view of the infinite 3D-structure formed by the different units of [NiCl(H$_2$O)$_2$(thpd)]Cl ([**7**]Cl) bonded by hydrogen bonds

plexed to group 10 metals. These ligands present different coordination environments, depending on the metal ion, as observed in the X-ray structures. Hence, coordination is N, S for Pd^{II} and Pt^{II}, but N, S, O for Ni^{II}. NMR studies proved very useful in determining the configuration of ligands in the complexes. These results will enable the study of the hemilabile behaviour of these novel N, O, S ligands when coordinated to transition metals.

Experimental Section

Generals Remarks: Preparations were performed using the usual vacuum line and Schlenk techniques. All reagents were commercial grade and were used without further purification. Acetonitrile was dried and distilled by standard methods and deoxygenated in the vacuum line.

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)ethyl 4-methylbenzenesulfonate[9] and 1-(2-mercaptoethyl)-3,5-dimethylpyrazole[10] were prepared according to published methods, as were samples of [PdCl$_2$(CH$_3$CN)$_2$][11] and [PtCl$_2$(CH$_3$CN)$_2$].[12]

Analyses (C, N, H, S) were performed in our analytical laboratory on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in 10^{-3} M absolute ethanol or acetonitrile solutions employing a Crison, micro CM 2200 conductimeter. Infrared spectra were recorded as KBr pellets or polyethylene mulls in the range 4000−100 cm^{-1} under a nitrogen atmosphere. Electronic spectra in solution were run on a Kontron-Uvikon 860 in acetonitrile between 750 and 350 nm. The ^{1}H and ^{13}C{^{1}H} NMR and HMQC spectra were obtained either on a Bruker AC-250 MHz or a Bruker 500 MHz instrument. ^{195}Pt{^{1}H} NMR spectra were obtained on a Bruker Advance DRX 250 MHz instrument. ^{1}H and ^{13}C chemical shifts (δ) were determined relative to internal TMS and are given in ppm. ^{195}Pt chemical shifts (δ) are relative to external 0.1 mol·dm^{-3} Na$_2$PtCl$_6$ and are given in ppm. Mass spectra were obtained on a HP 5989A apparatus.

Synthesis of 1-(3-Thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd): A solution of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl 4-methylbenzenesulfonate (6.26 g, 21.3 mmol), mercaptoethanol (1.50 mL, 21.2 mmol) and sodium hydroxide (0.94 g, 22.8 mmol) in distilled water (30 mL) was refluxed for 5 h. After cooling to room temperature, the reaction mixture was extracted with CH$_2$Cl$_2$ (3 × 25 mL). The collected organic layers were dried with anhydrous sodium sulfate and removed in vacuo to give a brown oil that was then washed with diethyl ether to afford the desired product as a white solid. Yield: 2.70 g (61%). M.p.: 46.6−47.5 °C. C$_9$H$_{16}$N$_2$OS (200.1) C 53.97, H 8.00, N 13.99, S 16.04; found C 54.17, H 7.93, N 14.10, S 15.91. IR (KBr, cm^{-1}): ν(O−H) 3221, ν(C−H)$_{al}$ 2943, ν(C=C), ν(C=N) 1549, δ(CH$_3$)$_{as}$ 1456, δ(CH$_3$)$_s$ 1386, δ(C−H)$_{oop}$ 792. ^{1}H NMR (250 MHz, CDCl$_3$ solution): δ = 2.20 (s, 3 H, *Me*), 2.25 (s, 3 H, *Me*), 2.60 (t, ^{3}J = 6 Hz, 2 H, *CH$_2$*−CH$_2$−OH), 2.95 (t, ^{3}J = 7 Hz, 2 H, pz-CH$_2$−*CH$_2$*), 3.28 (b, 1 H, OH), 3.69 (t, ^{3}J = 6 Hz, 2 H, CH$_2$−*CH$_2$*−OH), 4.14 (t, ^{3}J = 7 Hz, 2 H, pz-*CH$_2$*−CH$_2$), 5.79 (s, 1 H, pz-*CH*) ppm. ^{13}C{^{1}H} NMR (63 MHz, CDCl$_3$ solution): δ = 11.2 (*Me*), 13.5 (*Me*), 32.1 (pz-CH$_2$−*CH$_2$*), 35.6 (*CH$_2$*−CH$_2$−OH), 48.5 (pz-*CH$_2$*−CH$_2$), 61.2 (CH$_2$−*CH$_2$*−OH), 105.3 (pz-*CH*), 147.9 (pz-*C*) ppm. MS (CI, NH$_3$): *m/z* (%) = 201 [MH$^+$] (33%), 115 [pz-(CH$_2$)$_2$-S$^+$] (21), 109 [pz-CH$_2$$^+$] (88), 97 [pzH$^+$] (100).

1-(3-Thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd): A mixture of 1-(2-mercaptoethyl)-3,5-dimethylpyrazole (2.72 g, 17.4 mmol) and 3-chloro-1-propanol (1.50 mL, 17.4 mmol) in THF (40 mL) and sodium hydroxide (0.70 g, 17.0 mmol) in distilled water (30 mL) were refluxed for 4.5 h. After cooling to room temperature, the reaction mixture was extracted with CH$_2$Cl$_2$ (3 × 25 mL) and the collected organic layers were dried with anhydrous sodium sulfate and removed in vacuo. The brown oil thus formed was then washed with diethyl ether and the desired product precipitated as a white solid. Yield: 2.24 g (60%). M.p.: 53.7−54.1 °C. C$_{10}$H$_{18}$N$_2$OS (214.1) C 56.04, H 8.46, N 13.07, S 14.91; found C 55.83, H 8.21, N 12.82, S 14.73. IR (KBr, cm^{-1}): ν(O−H) 3298, ν(C−H)$_{al}$ 2913, ν(C=C), ν(C=N) 1553, δ(CH$_3$)$_{as}$ 1446, δ(CH$_3$)$_s$ 1386, δ(C−H)$_{oop}$ 778. ^{1}H NMR (250 MHz, CDCl$_3$ solution): δ = 1.80 (qt, 2 H, ^{3}*J* = 6 Hz, *CH$_2$*−CH$_2$−OH), 2.20 (s, 3 H, *Me*), 2.26 (s, 3 H, *Me*), 2.55 (t, ^{3}*J* = 6 Hz, 2 H, S-*CH$_2$*−CH$_2$−CH$_2$), 2.92 (t, ^{3}*J* = 7 Hz, 2 H, pz-*CH$_2$*−CH$_2$), 3.70 (t, ^{3}*J* = 6 Hz, 2 H, CH$_2$−*CH$_2$*−OH), 4.15 (t, ^{3}*J* = 7 Hz, 2 H, pz-*CH$_2$*−CH$_2$), 5.78 (s, 1 H, pz-*CH*) ppm. ^{13}C{^{1}H} NMR (63 MHz, CDCl$_3$ solution): δ = 11.2 (*Me*), 13.5 (*Me*), 28.6 (CH$_2$−*CH$_2$*−CH$_2$), 32.1, 32.2 (pz-CH$_2$−*CH$_2$*, S−*CH$_2$*−CH$_2$−CH$_2$), 48.5 (pz-*CH$_2$*−CH$_2$), 61.2 (CH$_2$−*CH$_2$*−OH), 105.2 (pz-*CH*), 139.3, 147.9 (pz-*C*) ppm. MS (CI, NH$_3$): *m*/*z* [%]: 215 [MH$^+$] (5%), 115 [pz-(CH$_2$)$_2$-S$^+$] (22), 109 [pz-CH$_2$$^+$] (59), 97 [pzH$^+$] (100).

Synthesis of [PdCl$_2$(L)] [L = thpd (1), L = thhd (2)] and [PtCl$_2$L] [L = thpd (3), L = thhd (4)]: A solution of [PdCl$_2$(CH$_3$CN)$_2$] (0.101 g, 0.389 mmol) or [PtCl$_2$(CH$_3$CN)$_2$] (0.075 g, 0.215 mmol) in acetonitrile (20 mL) was added dropwise to an equimolar solution of thpd or thhd in acetonitrile (10 mL). The resulting solution was stirred for 12 h, after which the acetonitrile was evaporated and the solid residue washed with chloroform (2 × 2 mL) and then dried under vacuum. The palladium complexes were orange solids, and the platinum complexes yellow solids.

Complex 1: Yield: 0.180 (99%). Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.01·10^{-3} M in acetonitrile): 1.8. C$_9$H$_{16}$Cl$_2$N$_2$OPdS (377.52) C 28.61, H 4.24, N 7.42, S 8.50; found C 28.23, H 4.11, N 7.13, S 8.26. IR (KBr, cm^{-1}): ν(O−H) 3386, ν(C−H)$_{al}$ 2984−2937, ν(C=C), ν(C=N) 1549, δ(CH$_3$)$_{as}$ 1468, δ(CH$_3$)$_s$ 1402, δ(C−H)$_{oop}$ 785. IR (polyethylene, cm^{-1}): ν(Pd−N) 467, ν(Pd−Cl) 340−335, ν(Pd−S) 292. ^{1}H NMR (500 MHz, [D$_3$]acetonitrile, 253 K): δ = 2.09 (b, 2 H, *CH$_2$*−CH$_2$−OH), 2.27 (s, 3 H, *Me*), 2.54 (s, 3 H, *Me*), 2.60 (b, 1 H, pz-CH$_2$−*CH*H), 3.20 (b, 1 H, pz-CH$_2$−*CH*H), 3.36 (t, 1 H, OH), 3.71 (b, 1 H, CH$_2$−*CH*H−OH), 3.83 (b, 1 H, CH$_2$−*CH*H−OH), 4.70 (b, 1 H, pz-*CH*H−CH$_2$), 4.84 (b, 1 H, pz-*CH*H−CH$_2$), 6.05 (s, 1 H, pz-*CH*) ppm. ^{13}C{^{1}H} NMR (63 MHz, [D$_3$]acetonitrile, 298 K): δ = 11.9 (*Me*), 15.4 (*Me*), 35.1, 42.6 (pz-CH$_2$−CH$_2$, *CH$_2$*−CH$_2$−OH), 49.8 (pz-*CH$_2$*−CH$_2$), 60.5 (CH$_2$−*CH$_2$*−OH), 109.2 (pz-*CH*) ppm.

Complex 2: Yield: 0.180 (96%). Conductivity (Ω^{-1} cm^2 mol^{-1}, 9.97·10^{-4} M in acetonitrile): 4.1. C$_{10}$H$_{18}$Cl$_2$N$_2$OPdS (391.62) C 30.64, H 4.60, N 7.15, S 8.20; found C 30.74, H 4.73, N 7.10, S 7.96. IR (KBr, cm^{-1}): ν(O−H) 3462, ν(C−H)$_{ar}$ 3123, ν(C−H)$_{al}$ 2975−2921, ν(C=C), ν(C=N) 1548, δ(CH$_3$)$_{as}$ 1463, δ(CH$_3$)$_s$ 1393, δ(C−H)$_{oop}$ 828. IR (polyethylene, cm^{-1}): ν(Pd−N) 462, ν(Pd−Cl) 343−329, ν(Pd−S) 307. ^{1}H NMR (500 MHz, [D$_3$]acetonitrile, 253 K): δ = 1.82 (b, 1 H, S−*CH*H−CH$_2$−CH$_2$), 2.21 (b, 1 H, S−*CH*H−CH$_2$−CH$_2$), 2.05 (b, CH$_2$−*CH$_2$*−CH$_2$), − this peak could not be integrated because it is too close to the solvent signal −2.39 (s, 3 H, *Me*), 2.51 (s, 3 H, *Me*), 2.51 (b, 1 H, pz-CH$_2$-*CH*H), 3.03 (b, 1 H, OH), 3.24 (b, 1 H, pz-CH$_2$−*CH*H), 3.52 (b, 1 H, CH$_2$−*CH*H−OH), 3.58 (b, 1 H, CH$_2$−*CH*H−OH), 4.73 (b, 1 H, pz-C*H*H−CH$_2$), 4.92 (b, 1 H, pz-C*H*H−CH$_2$), 6.11 (s, 1 H, pz-*CH*) ppm. ^{13}C{^{1}H} NMR (63 MHz, [D$_3$]acetonitrile, 298 K): δ = 12.0 (*Me*), 15.3 (*Me*), 32.3 (CH$_2$−*CH$_2$*−CH$_2$), 35.2, 37.6 (pz-CH$_2$−*CH$_2$*, S-*CH$_2$*−CH$_2$−CH$_2$), 49.8 (pz-*CH$_2$*−CH$_2$), 60.4 (CH$_2$−*CH$_2$*−OH), 109.3 (pz-*CH*), 145.0, 153.0 (pz-*C*) ppm.

Complex 3: Yield: 0.080 (98%). Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.07·10^{-3} M in acetonitrile): 5.3. C$_9$H$_{16}$Cl$_2$N$_2$OPtS (466.29) C 23.16, H 3.43, N 6.00, S 6.88; found C 23.03, H 3.48, N 6.02, S 6.73. IR (KBr, cm^{-1}): ν(O−H) 3420, ν(C−H)$_{al}$ 2974−2924, ν(C=C), ν(C=N) 1553, δ(CH$_3$)$_{as}$ 1470, δ(CH$_3$)$_s$ 1409, δ(C−H)$_{oop}$ 791. IR (polyethylene, cm^{-1}): ν(Pd−N) 496, ν(Pd-Cl) 327, ν(Pd−S) 303. ^{1}H NMR (500 MHz, [D$_3$]acetonitrile, 253 K): δ = 2.24 (b, 2 H, *CH$_2$*−CH$_2$−OH), 2.38 (s, 3 H, *Me*), 2.50 (s, 3 H, *Me*), 2.62 (b, 1 H, pz-CH$_2$−*CH*H), 3.22 (b, 1 H, pz-CH$_2$−*CH*H), 3.29 (t, 1 H, OH), 3.62 (m, 1 H, CH$_2$−*CH*H−OH), 3.76 (m, 1 H, CH$_2$−*CH*H−OH), 4.53 (m, 1 H, pz-*CH*H−CH$_2$), 4.72 (m, 1 H, pz-*CH*H−CH$_2$), 6.08 (s, 1 H, pz-*CH*) ppm. ^{13}C{^{1}H} NMR (63 MHz, [D$_3$]acetonitrile, 298 K): δ = 12.0 (*Me*), 15.0 (*Me*), 34.6 (pz-CH$_2$−*CH$_2$*), 43.5 (*CH$_2$*−CH$_2$−OH), 49.5 (pz-*CH$_2$*−CH$_2$), 60.2 (CH$_2$−*CH$_2$*−OH), 108.8 (pz-*CH*), 144.2 (pz-*C*) ppm. ^{195}Pt{^{1}H} NMR (53.8 MHz, [D$_3$]acetonitrile, 298 K): δ = −2868 ppm.

Complex 4: Yield: 0.083 (98%). Conductivity (Ω^{-1} cm^2 mol^{-1}, 9.85·10^{-4} M in acetonitrile): 6.4. C$_{10}$H$_{18}$Cl$_2$N$_2$OPtS (480.31) C 24.98, H 3.75, N 5.83, S 6.69; found C 25.25, H 3.81, N 6.11, S 6.62. IR (KBr, cm^{-1}): ν(O−H) 3477, ν(C−H)$_{ar}$ 3124, ν(C−H)$_{al}$ 2977−2924, ν(C=C), ν(C=N) 1549, δ(CH$_3$)$_{as}$ 1466, δ(CH$_3$)$_s$ 1397, δ(C−H)$_{oop}$ 828. IR (polyethylene, cm^{-1}): ν(Pd−N) 493, ν(Pd−Cl) 322, ν(Pd−S) 305. ^{1}H NMR (500 MHz, [D$_3$]acetonitrile, 253 K): δ = 1.86 (b, S−*CH*H−CH$_2$−CH$_2$), 2.31 (b, S−*CH*H−CH$_2$−CH$_2$), 1.93 (b, CH$_2$−*CH$_2$*−CH$_2$), last three peaks could not be integrated because they were too close to the solvent signal; 2.39 (s, 3 H, *Me*), 2.51 (s, 3 H, *Me*), 2.56 (b, 1 H, pz-CH$_2$−*CH*H), 3.09 (b, 1 H, OH), 3.28 (b, 1 H, pz-CH$_2$−*CH*H), 3.51 (m, CH$_2$−*CH$_2$*−OH), 3.55 (m, CH$_2$−*CH$_2$*−OH), last two peaks integrate together 2 H, 4.50 (m, 1 H, pz-C*H*H−CH$_2$), 4.82 (m, 1 H, pz-C*H*H−CH$_2$), 6.12 (s, 1 H, pz-*CH*) ppm. ^{13}C{^{1}H} NMR (63 MHz, [D$_3$]acetonitrile, 298 K): δ = 11.5 (*Me*), 14.4 (*Me*), 31.3 (CH$_2$−*CH$_2$*−CH$_2$), 34.4 (pz-CH$_2$−*CH$_2$*), 38.0 (S−*CH$_2$*−CH$_2$−CH$_2$), 49.0 (pz-*CH$_2$*−CH$_2$), 59.6 (CH$_2$−*CH$_2$*−OH), 108.3 (pz-*CH*), 143.6, 152.5 (pz-*C*) ppm. ^{195}Pt{^{1}H} NMR (53.8 MHz, [D$_3$]acetonitrile, 298 K): δ = −2879 ppm.

Synthesis of [NiCl$_2$(L)] with L = thpd (5), L = thhd (6): NiCl$_2$·6H$_2$O (0.546 mmol) in a mixture absolute ethanol (10 mL) and triethylorthoformate (2 mL) was added dropwise, under vigorous stirring, to a solution of thpd or thhd (0.546 mmol) in absolute ethanol (10 mL). The solution turned from initial green to yellow. After 12 h of stirring, the solvent was evaporated and the desired product obtained as a pale green solid.

Complex 5: Yield: 0.176 g (98%). Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.02·10^{-3} M in absolute ethanol): 18.7. C$_9$H$_{16}$Cl$_2$N$_2$NiOS (329.9) C 32.77, H 4.89, N 8.49, S 9.72; found C 32.68, H 5.06, N 8.20, S 9.43. IR (KBr, cm^{-1}): ν(O−H) 3269, ν(C−H)$_{al}$ 2947, ν(C=C), ν(C=N) 1555, δ(CH$_3$)$_{as}$ 1469, δ(CH$_3$)$_s$ 1401, δ(C−H)$_{oop}$ 724. IR (polyethylene, cm^{-1}):ν(Ni−O) 498, ν(Ni−N) 450, ν(Ni−Cl) 368, ν(Ni−S) 328. UV/Vis (absolute ethanol, 1.03·10^{-3} M), λ(ε): 422 nm (55 mol^{-1}cm^{-1}L).

Complex 6: Yield: 0.182 (97%). Conductivity (Ω^{-1} cm^2 mol^{-1}, 9.87·10^{-4} M in absolute ethanol): 14.3. C$_{10}$H$_{18}$Cl$_2$N$_2$NiOS (343.9) C 34.89, H 5.23, N 8.14, S 9.33; found C 34.66, H 5.17, N 7.86, S 9.07. IR (KBr, cm^{-1}): ν(O−H) 3250, ν(C−H)$_{al}$ 2922, ν(C=C), ν(C=N) 1558, δ(CH$_3$)$_{as}$ 1465, δ(CH$_3$)$_s$ 1387, δ(C−H)$_{oop}$ 728. IR (polyethylene, cm^{-1}): ν(Ni−O) 520, ν(Ni−N) 461, ν(Ni−Cl) 387, ν(Ni−S) 344. UV/Vis (absolute ethanol, 9.76·10^{-4} M), λ(ε): 414 nm (75 mol^{-1}cm^{-1}L).

Synthesis of [NiCl(H$_2$O)$_2$(thpd)]Cl ([7]Cl): Complex **5** (0.056 g, 0.170 mmol) was dissolved in ethanol or methanol. After 12 h, the solvent was evaporated and complex [**7**]Cl precipitated as bright green crystals.

Complex [7]Cl: Yield: 0.060 g (97%). Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.07·10^{-3} M in absolute ethanol): 41.3. C$_9$H$_{20}$Cl$_2$N$_2$NiO$_3$S (365.94) C 29.54, H 5.51, N 7.66, S 8.76; found C 29.60, H 5.46, N 7.72, S 8.56. IR (KBr, cm^{-1}): ν(O−H)$_{water}$ 3318, ν(O−H)$_{alcohol}$ 3238,

Table 4. Crystallographic data for **2**−**4**

Compound	**2**	**3**	**4**
Empirical formula	$C_{10}H_{18}Cl_2N_2OPdS$	$C_9H_{16}Cl_2N_2OPtS$	$C_{10}H_{18}Cl_2N_2OPtS$
Molecular mass	391.62	466.29	480.31
Temperature, K	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	Cc	$P2_1/n$
Unit cell dimensions			
a, Å	7.6360(10)	15.21(2)	7.6520(10)
b, Å	15.9160(10)	8.205(4)	15.9520(10)
c, Å	11.8370(10)	11.720(7)	11.8190(10)
β, deg	104.343(2)	111.59(8)	104.2740(10)
Volume, $Å^3$	1393.8(2)	1360(2)	1398.1(2)
Z	4	4	4
$D_{calcd.}$, $Mg \cdot m^{-3}$	1.866	2.277	2.282
μ, mm^{-1}	18.50	10.85	10.55
F(000)	784	880	912
Crystal size (mm)	0.1 × 0.1 × 0.2	0.2 × 0.2 × 0.1	0.1 × 0.1 × 0.3
θ range, deg	3.15 to 31.51	2.87 to 30.03	2.19 to 31.58
Reflexions collected: total, independent, R_{int}	3500, 1559, 0.0273	2015, 2015, 0.0153	8103, 3162, 0.0333
Data/restraints/parameters	1559/0/161	2015/2/145	3162/0/154
Weighting coef. a, b[a]	0.0522, 4.4364	0.0469, 0	0.0576, 0
Final R1, $wR2$	0.0359, 0.0954	0.0302, 0.0715	0.0281, 0.0787
R1 (all data), $wR2$	0.0388, 0.0982	0.0348, 0.0730	0.0369, 0.0815
Residual electron density, $e \cdot Å^{-3}$	+0.425, −0.451	+0.717, −0.743	+0.671, −0.622

[a] The function minimised was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (aP)^2 + bP]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$.

Table 5. Crystallographic data for [**7**]Cl

Compound	[**7**]Cl
Empirical formula	$C_9H_{20}Cl_2N_2NiO_3S$
Molecular mass	365.94
Temperature, K	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$ (n° 2)
Unit cell dimensions	
a, Å	7.206(3)
b, Å	8.611(8)
c, Å	12.661(5)
α, deg	95.97(5)
β, deg	104.97(3)
γ, deg	93.60(5)
Volume, $Å^3$	751.6(8)
Z	2
$D_{calcd.}$, $Mg \cdot m^{-3}$	1.617
μ, mm^{-1}	17.86
F(000)	380
Crystal size (mm)	0.1 × 0.1 × 0.2
θ range, deg	2.74 to 30.20
Reflexions collected: Total, independent, R_{int}	4333, 4333, 0.0099
Data/restraints/parameters	4333/0/184
Weighting coef. a, b[a]	0.0198, 0
Final $R1$, $wR2$	0.0357, 0.0610
$R1$ (all data), $wR2$	0.1029, 0.0726
Residual electron density, $e \cdot Å^{-3}$	+0.421, −0.347

[a] The function minimised was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (aP)^2 + bP]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$.

$\nu(C-H)_{al}$ 2957−2928, $\nu(C=C)$, $\nu(C=N)$ 1558, $\delta(CH_3)_{as}$ 1467, $\delta(CH_3)_s$ 1386, $\delta(C-H)_{oop}$ 728. IR (polyethylene, cm^{-1}): $\nu(Ni-O)$ 499, $\nu(Ni-N)$ 454, $\nu(Ni-Cl)$ 368, $\nu(Ni-S)$ 322. UV/Vis (absolute ethanol, $1.02 \cdot 10^{-3}$ M), λ(ε): 731 nm (4 $mol^{-1}cm^{-1}L$), 403 nm (10 $mol^{-1}cm^{-1}L$).

X-ray Crystallographic Study: Suitable crystals for X-ray diffraction experiments of compounds 2−4 and [7]Cl were obtained by crystallisation from methanol. Data for 2 and 4 were collected on a MAR345 diffractometer with an Image Plate detector, using the -scan technique. Data for 3 and [7]Cl were collected on an Enraf−Nonius CAD4 four-circle diffractometer, using the omega/2θ scan technique. All crystal data were collected using graphite-monochromated Mo-K_{α} radiation. The structures were solved by direct methods using the SHELXS-97 computer program[31] and refined by full-matrix least-squares method with a SHELXL-97.[32]

Fivc H atoms in structure [**7**]Cl were located from a difference synthesis and refined with an overall isotropic temperature factor. Thirteen Hs for [**7**]Cl and all hydrogen atoms for structures **2**−**4** were computed and refined using a riding model. The final R (on F) factor and ωR (on F^2) values, as well as the numbers of parameters refined and other details concerning the refinement of the crystal structure, are presented in Tables 4 and 5.

CCDC-199097 (**2**), -199096 (**3**), -199095 (**4**), and -199098 ([**7**]Cl) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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