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Inorganica Chimica Acta 355 (2003) 87–94

Inorganica Chimica Acta

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Synthesis, X-ray crystal structure, and NMR characterisation of thiolate-bridged dinuclear Ni(II), Pd(II) and Pt(II) complexes of didentate ligands with NS-donor set

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Received 29 January 2003; accepted 16 April 2003

Abstract

Thiolate-bridged dinuclear nickel(II), palladium(II) and platinum(II) complexes with *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed), $[MCl(med)]_2$ (M = Ni (**1**), Pd (**2**), Pt (**3**)), have been synthesised and characterised by elemental analyses, conductivity, IR, electronic spectra and NMR spectroscopies. The crystal structure of **2** was determined by a single-crystal X-ray diffraction method. The structure consists of thiolate-bridged dinuclear units. Each Pd(II) atom is coordinated by a pyrazolic nitrogen, one chlorine and two bridging sulfur atoms. When the synthesis of complex **1** was carried out in acetonitrile and in the presence of oxygen, $[NiCl_3(Hdeds)]$ (**4**) was formed (deds = 1,1′-(dithiodiethylene)bis(3,5-dimethylpyrazole)). The crystal structure of this complex was also determined by single-crystal X-ray diffraction method. The structure consists of nickel(II) ions coordinated by three chloride ions and one pyrazolic nitrogen atom. Ligand deds is the result of the oxidation of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed).

Keywords: Nickel; Palladium; Platinum; Dinuclear; N,S ligands

1. Introduction

The known tendency of thiolate ligands to give highly insoluble neutral complexes of polymeric nature has led to new synthetic strategies [1] and thus has enabled the obtaining of structural information on metal-thiolate complexes [2].

Discrete first-row transition-metal complexes featuring central $M(\mu_2\text{-SR})_xM$ cores ($x = 1–3$) have come under increased investigation in the past several years [3]. There are several $M(\mu_2\text{-SR})_xM$ type complexes [4], most of which have been studied in attempts to mimic the bonding, spectral and redox properties of bioinorganic compounds [1a,5,6,7].

The $Ni(\mu_2\text{-SR})_xNi$ has attracted much attention to model the active site of the nickel-enzymes [8], in particular for the hydrogenases, metalloenzymes which catalyse $H_2 = 2H^+ + 2e^-$. Only recently, however, it has been established that the active site contained a dimetallic substructure [9].

$Pt(\mu_2\text{-SR})_xPt$ complexes have been ascribed as antitumor drugs [10]. However, their inactivation is thought probably to be due to the bonding of platinum atoms to sulfur-containing biomolecules [11].

In recent years, we have studied and reported the synthesis and characterisation of ligands *N*-alkylaminopyrazole [12], *N*-hydroxyalkylpyrazole [13], *N*-phosphinopyrazole [14] and more recently ligands containing pyrazolyl and thioether groups [15].

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doi:10.1016/S0020-1693(03)00333-5

In the present paper, we describe the examination of dinuclear Ni(II), Pd(II) and Pt(II) complexes of the ligand with NS-donor set *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed). The reactivity of dinuclear Ni(II) complex in acetonitrile with the HCl formed in the reaction mixture in the presence of oxygen, leads to a new mononuclear Ni(II) complex with a $NiCl_3N$ core. Thiolate ligands med^- are oxidised to disulfide 1,1′(dithiodiethylene(bis(3,5-dimethylpyrazole) (deds) in this reaction (Fig. 1).

NMR studies of complexes **1**–**3** and the X-ray crystal structures of **2** and **4** are also presented.

2. Results and discussion

2.1. Synthesis and spectroscopic properties of the complexes

The *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed) (Fig. 2) was synthesised according to a procedure previously described by Bouwman et al. [16]. Complexes $[M(med)Cl]_2$ (M = Ni(II) (**1**), Pd(II) (**2**) and Pt(II) (**3**)) were obtained by reaction of the ligand Hmed with $NiCl_2 \cdot 6H_2O$, $[PdCl_2(CH_3CN)_2]$ [17] or $[PtCl_2(CH_3CN)_2]$ [18], respectively. Reaction of Hmed with $NiCl_2 \cdot 6H_2O$ always gave a secondary product (**4**) in very small quantities. This compound (**4**) was formulated as $[NiCl_3(Hdeds)]$ being deds 1,1′-(dithiodiethylene)bis(3,5-dimethylpyrazole), the product of oxidation of med^-. Complex $[NiCl_3(Hdeds)]$ (**4**) was obtained directly by treatment of $NiCl_2 \cdot 6H_2O$ with Hmed in acetonitrile, in the presence of oxygen.

Elemental analyses of products **1**–**4** are consistent with the proposed molecular formula. Conductivity values in acetonitrile for all complexes are in agreement with a non-electrolyte nature of complexes. The reported values for 10^{-3} M solutions of non-electrolyte complexes in acetonitrile are lower than 120 Ω^{-1} cm^2 mol^{-1} [19].

The main difference among IR spectra of complexes **1**–**3** and the IR spectrum of the free ligand is the absence of the ν(S–H) band found at 2543 cm^{-1}. This happens because ligand Hmed acts as a thiolate when complexed. Complexes **1**–**3** present one band between 1550–1554 cm^{-1} which is characteristic of ν(C=C) and ν(C=N) absorption bands of pyrazole rings. However, complex **4** shows two absorption bands in this region (1592 and 1554 cm^{-1}), which were assigned to the protonated and complexed pyrazolyl groups, respectively [20].

The IR spectra of complexes in the region 500–100 cm^{-1} were also studied [21]. Complexes **1**–**3** show three well-defined bands corresponding to ν(M–S) at 366–315 cm^{-1}, ν(M–Cl) at 388–333 cm^{-1} and ν(M–N) at 513–450 cm^{-1}. For complex **4** only two bands were assigned for ν(Ni–Cl) at 375 cm^{-1} and ν(Ni–N) at 484 cm^{-1}.

Electronic spectra of the complexes **1** and **4** were measured in acetonitrile. Complex **1** shows two intense ligand-to-metal charge transfer bands at 524 nm ($\varepsilon = 411$ mol^{-1} $cm^{-1}l$) and 416 nm ($\varepsilon = 1010$ l mol^{-1} cm^{-1}) [22]. Electronic spectrum of complex **4** exhibits one d–d band at 616 nm ($\varepsilon = 215$ l mol^{-1} cm^{-1}), which can be attributed to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition, characteristic for tetrahedral Ni(II) complexes. Absorption bands at 447 and 362 nm for **2** and 384 nm for **3** can be assigned to d–d and charge transfer transitions [23].

2.2. NMR experiments

^1H and ^{13}C NMR spectra of compounds **1**, **2** and **3** were recorded in $CDCl_3$ and show the signals of the coordinated ligands. NMR data are reported in the experimental section. From the structure of complexes **1**, **2** and **3** it can be seen that the two protons of each CH_2 in the $S–CH_2–CH_2–N$ chain are diastereotopic, thus leading to four groups of signals, which can be associated to a single hydrogen each. This happens because of the rigid conformation of the ligand when it is complexed. In this way, each group of signals can be assigned as doublets of doublets of doublets (Fig. 2).

HMQC spectra (Fig. 3) were used to assign protons H_{1R} and H_{1S} to the two doublets of doublets of doublets of lower δ and H_{2R} and H_{2S} to those of higher δ.

NOESY spectra (Fig. 4) allowed us to differentiate H_{2R} from H_{2S} and $CH_3(4)$ from $CH_3(7)$: the singlet that appears at 2.56 ppm shows NOE interaction only with H_5 and was assigned to $CH_3(4)$. The singlet at 2.29 ppm, besides having NOE interaction with H_5, shows strong NOE interaction with the doublets of doublets of

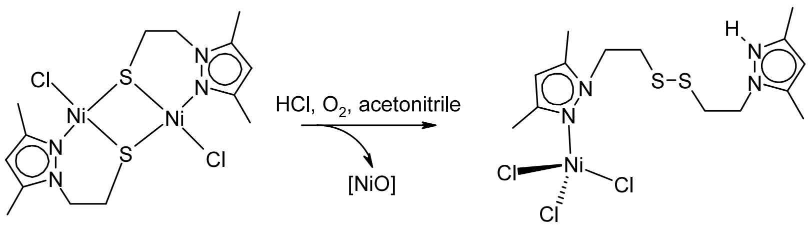

Fig. 1. Synthesis of $[NiCl_3(Hdeds)]$ (**4**).

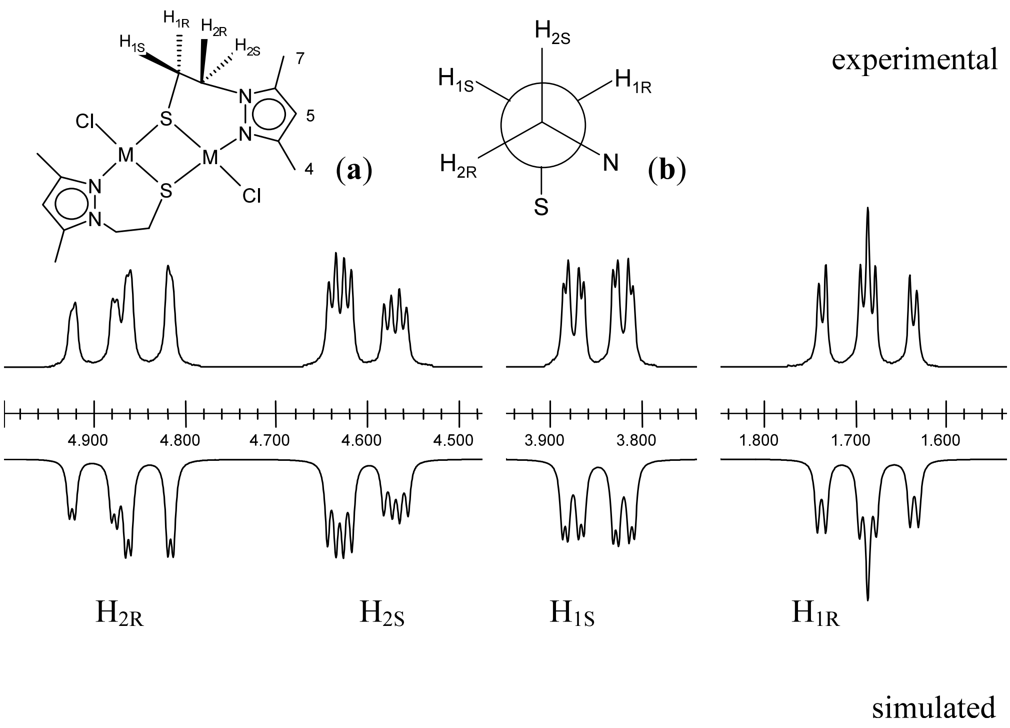

Fig. 2. The 400 MHz ^{1}H NMR and gNMR simulated spectra for NCH_2CH_2S fragment of $[PdCl(med)]_2$ (**2**), including (a) the numbering and (b) the dihedral angles for the NCH_2CH_2S fragment of $[MCl(med)]_2$ (M = Ni (**1**), Pd (**2**) or Pt (**3**)).

doublets at 4.60 ppm and weak NOE interaction with the doublets of doublets of doublets at 4.87 ppm and was assigned to $CH_3(7)$. From the X-ray structure of **2**, it can be seen that the nearest proton to $CH_3(7)$ is H_{2S} and therefore should have a stronger NOE interaction. This information leads us to assign it to the doublets of doublets of doublets at 4.60 ppm and H_{2R} to the signal at 4.87 ppm.

Coupling constants (obtained from the gNMR generated ^{1}H NMR simulated spectra, Fig. 2) helped us to differentiate H_{1R} and H_{1S}. These coupling constants agree with the conformation of the $S–CH_2–CH_2–N$ chain as seen in Fig. 2, which has been corroborated by a X-ray crystal study.

Geminal ^2J and ≈180° ^3J coupling constants have significantly higher values than ≈30° and ≈60° ^3J

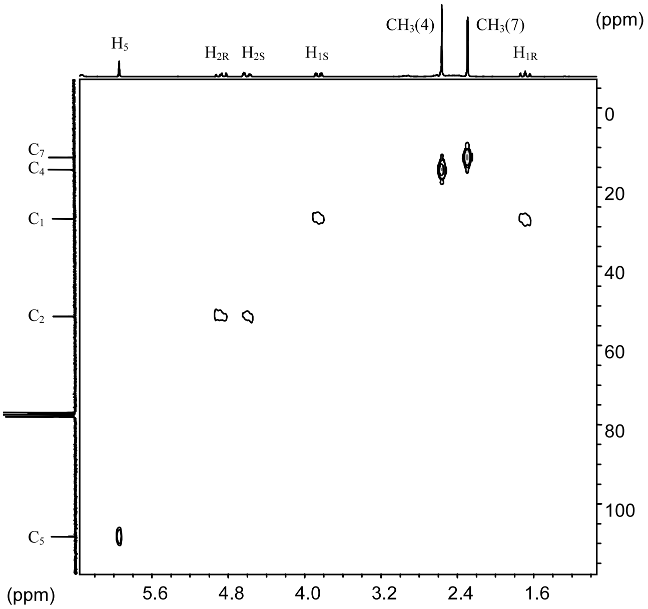

Fig. 3. The 250 MHz 2D HMQC spectrum of $[PdCl(med)]_2$ (**2**).

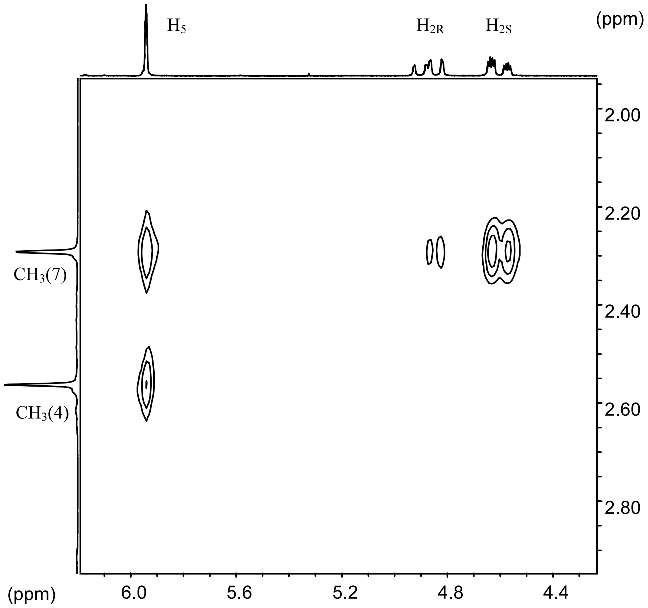

Fig. 4. The 250 MHz 2D NOESY spectrum of $[PdCl(med)]_2$ (**2**).

Table 1
${}^1H$ NMR results: chemical shifts (ppm) and ${}^1H-{}^1H$ coupling constants (Hz)

Compound	**1** ($CDCl_3$)	**2** ($CDCl_3$)	**3** ($CDCl_3$)
δ H (2S)	4.49	4.60	4.27
δ H (2R)	5.60	4.87	5.00
δ H (1R)	0.75	1.69	1.67
δ H (1S)	2.63	3.85	3.97
${}^2J$(2R,2S)	– 14.8	– 15.4	– 14.9
${}^2J$(1R,1S)	– 13.2	– 13.9	– 13.7
${}^3J$(1R,2S)	2.2	2.2	2.1
${}^3J$(1S,2S)	3.7	4.4	4.0
${}^3J$(1R,2R)	11.7	11.7	11.6
${}^3J$(1S,2R)	1.5	1.5	1.8
${}^3J$(Pt,1R)	–	–	45.0
${}^3J$(Pt,1S)	–	–	49.8

coupling constants [24] (Fig. 2). Thus, H_{1R} should correspond to the doublets of doublets of doublets at 1.69 ppm and H_{1S} to the one at 3.85 ppm (Table 1).

2.3. Crystal and molecular structure of $[Pd(med)Cl]_2$ (**2**)

The structure of **2** (Fig. 5) consists of dimeric $[Pd(med)Cl]_2$ units linked by van der Waals forces. Each palladium atom is coordinated by two thiolate-bridging sulfurs (in *anti* conformation), one pyrazole nitrogen and one chloride ion in a distorted square-planar geometry. Table 2 lists some selected bond distances and bond angles for this complex.

The largest deviations to the mean planes that contain the four donor atoms and the Pd atom are 0.052(1) Å in S(2) and – 0.048(3) Å in N(3) for Pd(2) and 0.062(3) Å in N(2) and – 0.068(1) in S(1) for Pd(1).

The two planar $PdClNS_2$ units are joined via two bridging thiolate ligands forming a four-membered ring, which is CR-form with Pd···Pd and S···S distances 3.1174(4) and 2.910(1) Å, respectively. The dihedral angles between the planes Pd(1)–S(1)–Pd(2) and Pd(1)–S(2)–Pd(2) is 54.84(4)°. This dihedral angle is larger than those found in the literature for dimeric complexes with $PdClNS_2$ core [6c–6d].

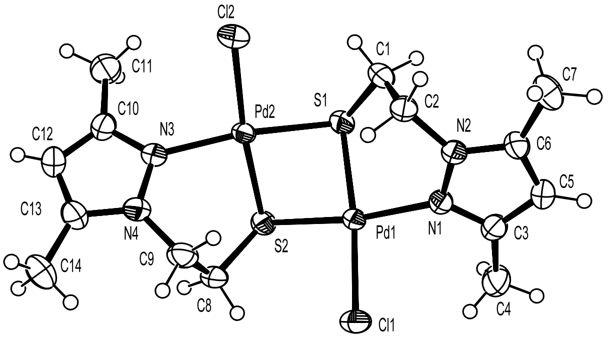

Fig. 5. ORTEP drawing of $[PdCl(med)]_2$ (**2**) (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

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

2		**4**	
Bond lenths			
Pd(1)–N(1)	2.057(3)	Ni–N(1)	2.011(3)
Pd(1)–S(1)	2.2804(10)	Ni–Cl(1)	2.2916(11)
Pd(1)–S(2)	2.2807(9)	Ni–Cl(2)	2.2492(12)
Pd(1)–Cl(1)	2.3379(10)	Ni–Cl(3)	2.2386(12)
Pd(1)–Pd(2)	3.1175(4)		
Pd(2)–N(3)	2.056(3)		
Pd(2)–S(2)	2.2746(10)		
Pd(2)–S(1)	2.2864(10)		
Pd(2)–Cl(2)	2.3409(12)		
Bond angles			
N(1)–Pd(1)–S(1)	91.51(10)	N(1)–Ni–Cl(1)	104.79(9)
N(1)–Pd(1)–S(2)	170.42(10)	N(1)–Ni–Cl(2)	105.13(9)
S(1)–Pd(1)–S(2)	79.29(4)	N(1)–Ni–Cl(3)	119.41(9)
N(1)–Pd(1)–Cl(1)	93.49(10)	Cl(1)–Ni–Cl(2)	105.29(5)
S(1)–Pd(1)–Cl(1)	173.65(4)	Cl(1)–Ni–Cl(3)	105.21(5)
S(2)–Pd(1)–Cl(1)	95.87(4)	Cl(2)–Ni–Cl(3)	115.67(5)
N(3)–Pd(2)–S(2)	92.06(9)		
N(3)–Pd(2)–S(1)	171.24(9)		
S(2)–Pd(2)–S(1)	79.29(4)		
N(3)–Pd(2)–Cl(2)	93.20(9)		
S(2)–Pd(2)–Cl(2)	173.54(4)		
S(1)–Pd(2)–Cl(2)	95.52(4)		

Pd–N distances are smaller and Pd–Cl and Pd–S distances are similar to the ones found for related complexes [6]. However, Pd–N bond distances are of the same order as the ones found in the literature for complexes containing Pd–Npz (pz = pyrazole) [13,15].

The pyrazole–thiolate ligand acts as a bidentate chelate (as well as bridging ligand), forming two Pd–S–C–C–N–N rings. These two six-membered rings have boat conformation. Bite angles S(1)–Pd(1)–N(1) and N(3)–Pd(2)–S(2) are 91.5(1)° and 92.1(1)°, respectively.

The distortion of the boat in six-membered rings are $\Delta C_S(Pd1) = 10.1(3)°$, $\Delta C_2(S1-C1) = 42.4(4)°$ and $\Delta C_S(Pd2) = 13.1(3)°$, $\Delta C_2(S2-C8) = 40.5(4)°$ for Pd1–S1–C1–C2–N2–N1 and Pd2–S2–C8–C9–N4–N3, respectively.

2.4. Crystal and molecular structure of $[NiCl_3(Hdeds)]$ (**4**)

The structure of **4** consists of discrete $[NiCl_3(Hdeds)]$ units, linked by hydrogen bonds (Fig. 6). Nickel atom is coordinated by three terminal chloride ions and one pyrazole nitrogen in a slightly distorted tetrahedral geometry.

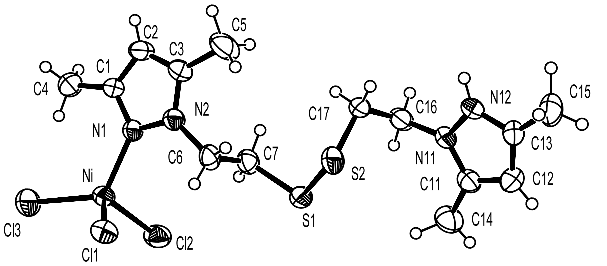

Fig. 6. ORTEP drawing of [NiCl$_3$(Hdeds)] (**4**) (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

Ni–N and Ni–Cl distances are similar to those found in the literature for Ni(II) complexes containing pyrazolyl groups and at least one coordinated Cl atom [25].

The azine nitrogen in the uncoordinated pyrazole (N12) is protonated. The positive charge is cancelled out by the negative charge that is provided by the third chloride ion linked to Ni(II), forming a zwitterionic structure. Pyrazole N(12) atom is intermolecularly hydrogen bridged to Cl(1) atom from another molecule, thereby linking the molecules into a chain (the N(12)–H bond length is 0.86(4) Å and the contact parameters between N(12)–H and Cl(1) are: H···Cl(1), 2.30(4) Å; N(12)···Cl(1), 3.158(4) Å; symmetry code (i): x, y, $1+z$).

No other complex with NiCl$_3$N core (terminal Cl) has been fully described in the literature. Only one complex with this core (but with one bridged chloride ion) was found, but due to the poor quality of the crystal it could not be further described in the corresponding paper [26].

The most similar complex to the one presented here is a copper complex with CuCl$_3$N core (pyrazole nitrogen and terminal chloride): [Cu(daeH)Cl$_3$] where daeH = *N*-(2-(3,5-dimethyl-1-pyrazolyl)ethyl)hydro-ethylammonium [27].

3. Experimental

3.1. Generals methods

Preparations were performed using usual *vacuum* line and Schlenk techniques. All reagents were commercial grade materials and were used without further purification. Acetonitrile and dichloromethane were dried and distilled by standard methods and previously deoxygenated in the *vacuum* line.

N-(2-mercaptoethyl)-3,5-dimethylpyrazole was prepared according to the published methods [16].

Samples of [PdCl$_2$(CH$_3$CN)$_2$] [17] and [PtCl$_2$(CH$_3$CN)$_2$] [18] were prepared as described in the literature.

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 acetonitrile solutions employing a Crison, micro CM 2200 conductimeter. Infrared spectra were recorded from 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 NMR, ^{13}C{^{1}H} NMR, HMQC and NOESY spectra were obtained either on a Bruker 250 MHz or Bruker 400 MHz instrument. Chemical shifts (δ) were determined relative to internal TMS and are given in ppm.

3.2. Synthesis

3.2.1. Preparation of [Ni(med)Cl]$_2$ (1)

To a solution of 0.345 g (2.21 mmol) of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole in 5 ml of absolute ethanol (light brown) and 2 ml of triethyl ortoformate was added dropwise a solution of 0.525 g (2.21 mmol) of NiCl$_2$·6H$_2$O in absolute ethanol (green). Solution turned into dark brown colour and a precipitate of the same colour was formed. After stirring for 1 h, the precipitate was filtered off and dried in vacuum. Yield: 0.46 g (83%), $C_{14}H_{22}Cl_2N_4Ni_2S_2$ (498.78): C 33.71, H 4.45, N 11.23, S 12.86; Found: C 34.06, H 4.46, N 11.24, S 12.53%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.06 10^{-3} M in acetonitrile): 14.0, IR (KBr, cm^{-1}): ν(C–H)$_{al}$ 2982–2921, ν(C=C), ν(C=N) 1554, δ(CH$_3$)$_{as}$ 1469–1421, δ(CH$_3$)$_s$ 1310, δ(C–H)$_{oop}$ 774. IR (polyethylene, cm^{-1}): ν(Ni–N)$_{as}$ 463, ν(Ni–Cl) 388, ν(Ni–S) 366. UV–Vis (acetonitrile, 1.1 10^{-3} M, nm), $\lambda(\varepsilon)$: 524(411), 416(1010). ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 2.19$ (s, 6H, *Me*), 2.74 (s, 6H, *Me*), 0.72/2.60/4.47/5.58 (4 ddd, 8H, pz–*CH$_2$*–*CH$_2$*), 5.79 (s, 2H, pz–*CH*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) $\delta = 11.9$ (*Me*), 15.7 (*Me*), 24.7 (S–*CH$_2$*–CH$_2$), 50.4 (pz–*CH$_2$*–CH$_2$), 108.4 (pz–CH), 142.1, 152.8 (pz–C).

3.2.2. Preparation of [Pd(med)Cl]$_2$ (2) and [Pt(med)Cl]$_2$ (3)

A solution of 0.100 g (0.39 mmol) of [PdCl$_2$(CH$_3$CN)$_2$] (orange) or 0.076 g (0.22 mmol) of [PtCl$_2$(CH$_3$CN)$_2$] (yellow) in 5 ml of dichloromethane was added dropwise to a solution containing (Pd: 0.061 g, 0.39 mmol; Pt: 0.034 g, 0.22 mmol) of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole in 5 ml of dichloromethane (light brown). After 12 h stirring, solvent was removed in vacuum. For Pd complex, the resulting precipitate was then filtered off and washed with diethyl ether, yielding the desired compound. Pt complex was further purified by chromatography (silica gel 60) using methanol-dichloromethane (1:9) as eluent to give the desired product as a yellow precipitate.

2: Yield: 0.112 g (98%), $C_{14}H_{22}Cl_2N_4S_2Pd_2$ (594.23): C 28.30, H 3.73, N 9.43, S 10.76; Found: C 28.65, H 3.91, N 9.20, S 10.44%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 7.08 10^{-4} M in acetonitrile): 11.2, IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3119–3078, ν(C–H)$_{al}$ 2976–2918, ν(C=C), ν(C=N) 1550, δ(CH$_3$)$_{as}$ 1466–1422, δ(CH$_3$)$_s$ 1312, δ(C–H)$_{oop}$ 814–771. IR (polyethylene, cm^{-1}): ν(Pd–N)$_{as}$ 450, ν(Pd–Cl) 360, ν(Pd–S) 315. UV–Vis (acetonitrile, 1.0 10^{-3} M, nm), λ: 447, 362. ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 2.29$ (s, 6H, *Me*), 2.56 (s, 6H, *Me*), 1.69/3.85/4.60/4.87 (4 ddd, 8H, pz–*CH$_2$*–*CH$_2$*), 5.94 (s, 2H, pz–*CH*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) $\delta =$ 12.4 (*Me*), 15.6 (*Me*), 28.0 (S–*CH$_2$*–CH$_2$), 52.6 (pz–*CH$_2$*–CH$_2$), 108.2 (pz–CH), 141.9, 152.4 (pz–C).

3: Yield: 0.044 g (52%), $C_{14}H_{22}Cl_2N_4S_2Pt_2$ (771.54): C 21.79, H 2.87, N 7.26, S 8.32; Found: C 21.67, H 2.52, N 6.99, S 8.03%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.13 10^{-3} M in acetonitrile): 12.5, IR (KBr, cm^{-1}): ν(C–H)$_{al}$ 2959–2853, ν(C=C), ν(C=N) 1552, δ(CH$_3$)$_{as}$ 1467–1416, δ(CH$_3$)$_s$ 1302, δ(C–H)$_{oop}$ 801. IR (polyethylene, cm^{-1}): ν(Pt–N)$_{as}$ 513, ν(Pt–Cl) 330, ν(Pt–S) 320. UV–Vis (acetonitrile, 1.6 10^{-3} M, nm), λ: 384. ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 2.23$ (s, 6H, *Me*), 2.54 (s, 6H, *Me*), 1.69/3.98/4.29/5.02 (4 ddd, 8H, pz–*CH$_2$*–*CH$_2$*), 5.94 (s, 2H, pz–*CH*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) $\delta = 12.3$ (*Me*), 14.9 (*Me*), 24.8 (S–*CH$_2$*–CH$_2$), 51.1 (pz–*CH$_2$*–CH$_2$), 107.7 (pz–CH), 141.1, 152.2 (pz–C).

3.2.3. Preparation of [NiCl$_3$(Hdeds)] (4)

A solution of 0.256 g (1.1 mmol) of NiCl$_2$·6H$_2$O in 20 ml of acetonitrile (blue) was added dropwise to a solution of 0.168 g (1.1 mmol) of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole in 5 ml of acetonitrile and 2 ml of triethyl ortoformate. Solution turned into dark brown colour (dimeric nickel(II) complex). In presence of oxygen, and after 3 days, solution turned into blue turquoise and a pale yellow precipitate was formed (nickel oxide). Precipitate was filtered off and then solvent was evaporated to give the desired product. Yield: 0.24 g (96%), $C_{14}H_{23}Cl_3N_4NiS_2$ (476.54): C 35.29, H 4.86, N 11.76, S 13.46; Found: C 35.56, H 4.94, N 11.83, S 13.52%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.01 10^{-3} M in acetonitrile): 21.4, IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3129, ν(C–H)$_{al}$ 2967–2920, ν(C=C), ν(C=N) 1592, 1554, δ(CH$_3$)$_{as}$ 1462–1427, δ(CH$_3$)$_s$ 1292, δ(C–H)$_{oop}$ 815–833. IR (polyethylene, cm^{-1}): ν(Ni–N)$_{as}$ 484, ν(Ni–Cl) 375. UV–Vis (acetonitrile, 9.8 10^{-4} M, nm), $\lambda(\varepsilon)$: 616(215).

3.3. X-ray crystal structure analyses

Suitable crystals for X-ray diffraction experiments of compounds **2** and **4** were obtained by crystallisation from CH$_2$Cl$_2$ and acetonitrile, respectively. Data were collected on a MAR345 diffractometer with Image Plate detector, using φ-scan technique. Both crystals were collected with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods using the SHELXS 97 computer program [28] and refined by full-matrix least-squares method with a SHELXL 97 computer program [29].

Table 3
Crystallographic data for **2** and **4**

Compound	**2**	**4**
Empirical formula	$C_{14}H_{22}Cl_2N_4Pd_2S_2$	$C_{14}H_{23}Cl_3N_4NiS_2$
Molecular mass (g)	594.18	476.54
Temperature (K)	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions		
a (Å)	8.649(1)	10.545(1)
b (Å)	10.484(1)	10.488(1)
c (Å)	11.946(1)	10.944(1)
α (°)	104.685(1)	82.961(2)
β (°)	95.166(1)	71.510(1)
γ (°)	95.912(1)	64.282(2)
V Å^3	1034.64(2)	1034.0(2)
Z	2	2
D_{calc} (g cm^{-3})	1.907	1.531
μ (mm^{-1})	2.202	1.532
F(0 0 0)	584	492
Crystal size (mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
θ Range (°)	3.03–31.50	1.96–24.89
Reflexions collected:		
Total, independent, R_{int}	9823, 5922, 0.0266	5688, 3146, 0.0287
Data/restraints/parameters	5381, 0, 243	3146, 0, 297
a/*b* *	0.0413, 2.6258	0.0487, 1.3308
Final R_1, wR_2	0.0370, 0.0902	0.0392, 0.0969
R_1 (all data), wR_2	0.0487, 0.0975	0.0577, 0.1061
Residual electron density (e Å^{-3})	+0.756, −0.843	+0.310, −0.398

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

All hydrogen atoms 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 Table 3.

4. Conclusion

The ligand *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed) reacts with Ni(II), Pd(II) and Pt(II) ions to give new thiolate bridged dinuclear compounds. These complexes contain the anionic [med]$^-$ ligand in a chelating form, which induces a rigid conformation of the ethylenic fragment. NMR studies have shown to be very useful in the determination of the configuration of ligands in these complexes. This study represent an important addition to the series of similar structures established with M(μ$_2$-SR)$_2$M cores. Ni(II) complex

$[NiCl(med)]_2$ can be oxidised in acetonitrile solution leading to a new complex with an unique $NiCl_3N$ core.

We expect to find further exciting reactivity of **2** with other substrates to permit study of the hemilabile character of the ligand.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 196720 (**2**), CCDC 196721 (**4**). These data can be obtained free of charge at www: http://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].

Acknowledgements

Supports by the Ministerio de Educación y Cultura of Spain (Project BQU2000-0238 and grant to J.G.) are gratefully acknowledged.

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