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Synthesis, crystal structures and use in ethylene oligomerization catalysis of novel mono- and dinuclear nickel complexes supported by (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide ligand

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ABSTRACT

The coordination chemistry of Ni^{II} supported by (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide ligand (**HL**) is reported and discussed. The crystal structure of ligand **HL** has been determined as well as those of three new Ni^{II} complexes ($Ni(HL)_2Br_2$, NiL_2 and μ-aquo-Ni_2L_4). The pseudo-octahedral bis(chelate) Ni(II) complex **2** (NiL_2), in which unexpected and singular Ni···S interaction is observed, was evaluated as catalyst for the oligomerization of ethylene and found to provide ethylene dimers and trimers as primary products with a turnover frequency (TOF) of 31 200 mol of C_2H_4 per mol. of Ni and per hour.

1. Introduction

We earlier reported interesting magnetic properties of transition metal complexes supported by 2-salicyloylhydrazono-1,3-dithiolane ($\mathbf{H_2L}^*$) and its derivatives [1–7]. For instance, the dinuclear complex $Mn_2(\mathbf{HL}^*)_4(\mu\text{-}OCH_3)_2$ was found to exhibit the largest *J* value ($J = +19.7\ cm^{-1}$) reported so far for a Mn^{III}–Mn^{III} ferromagnetic interaction [2]. On this basis, we have been working on slight modifications of the organic peripheral backbone as well as on using other metal centres, such as chromium [5], iron [3,7] and cobalt [6].

When exploring the iron chemistry with such hydrazine derivative ligands, we also observed an unusual spontaneous reduction from Fe^{III} to Fe^{II} of the mononuclear complexes [3]. This possible photo-induced redox reaction was subsequently fully investigated by electrochemistry, EPR studies, magnetic measurements, as well as solid-state molecular structure determinations. Such a phenomenon opens up new research opportunities, as recently pointed out by Wernsdorfer and co-worker [8] and demonstrated by our patent [9].

With the purpose of acquiring more insight into the structural factors controlling and influencing the formation and stabilization of dinuclear complexes [2,7] in the crystalline state (with possible impact on their magnetic behaviour) and also due the spontaneous reduction of Fe^{III} to Fe^{II} observed in iron mononuclear species, the original ligand was modified at specific positions (see Scheme 1). We have also become interested in studying the coordination chemistry of this type of hydrazine ligands with other transition metals, along with their possible applications as catalysts. In the present article, we report the synthesis and structural characterisation of novel Ni^{II} complexes supported by the (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide ligand (Scheme 1) and their subsequent use in ethylene oligomerization catalysis.

2. Experimental

2.1. General procedures

All manipulations were performed under aerobic conditions unless specified otherwise. Reagents and solvents were commercially purchased and used as received. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^1H, 300 MHz; ^{13}C, 75.47 MHz). Assignments were based on ^1H, ^1H-COSY, ^1H, ^{13}C-HMQC and ^1H, ^{13}C-HMBC experiments. IR spectra were recorded in the region 4000–100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg.

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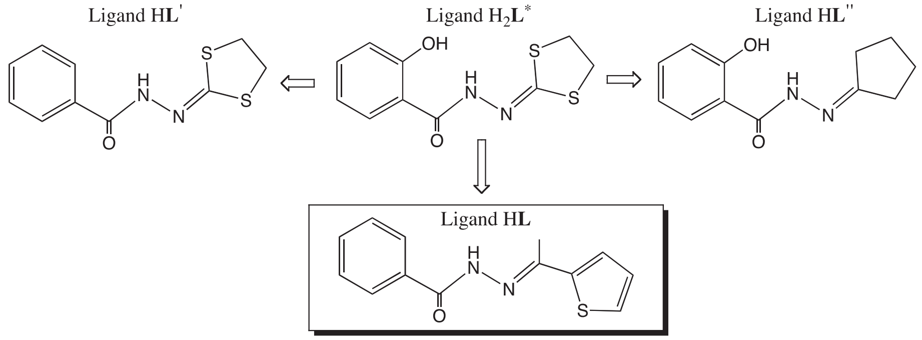


Scheme 1. Structural relationship between H**L** ((*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide) and H_2**L*** (2-salicyloylhydrazono-1,3-dithiolane). The ligands H**L**′, and H**L**″ have been previously described [4,7].

2.2. Synthesis of (E)-N′-(1-(thiophen-2-yl)ethylidene)benzohydrazide (HL)

Benzhydrazide (5.00 g, 36.7 mmol) and 2-acetylthiophene (4.63 g, 36.7 mmol) were placed in a quartz tube in a QV-50S reactor equipped with temperature and pressure probes, which was introduced in the microwave oven (Milestone Micro-SYNTH apparatus). The reaction proceeded under stirring for 4.5 min at 200 W, with a final temperature of 247 °C and final pressure of 8.0 bar. The system was then allowed to cool down to room temperature, leading to crystallization of the hydrazone. Ethyl ether was added to the quartz tube to wash the product which was filtrated under reduced pressure and further washed with diethyl ether to afford 8.30 g (93%) of yellowish needles (m.p. 188–189 °C). ^{1}H NMR (d_6-DMSO): δ 2.39 (s, 3H, CH_3), 7.11 (s, 1H, Thio-H), 7.69-7.38 (m, 4H, 2 × Thio-H and 2 × Ar–H), 7.87 (s, 2H, Ar–H), 10.79 (br s, 1H, N–H). $^{13}C\{^{1}H\}$ NMR (d_6-DMSO): δ 14.9 (CH_3), 127.5 (C-Thio), 127.7 (C-Thio), 128.2 (C-Thio), 129.0 (C-Thio), 131.4 (C–Ar), 143.1(C–Ar), 152.6 (C=N), 163.4 (C=O). IR (pure, orbit diamond): 1652 (C=O), 1637 (N–H), 1541(C=N). *Anal.* Calc. for $C_{13}H_{12}N_2OS$: C, 63.91; H, 4.95; N, 11.47. Found: C, 63.95; H, 4.94; N, 11.54%.

2.3. Synthesis of complex **1** [Ni(HL)$_2$(Br)$_2$]

To a solution of $Ni(Br)_2(PPh_3)_2$ (0.15 g, 0.20 mmol) in THF (20 mL), (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide (0.1 g, 0.41 mmol) was added. The green solution was left under stirring overnight at room temperature and then filtered. Green powder of the titled complex was obtained after solvent evaporation and then dried under vacuum. Green monocrystals suitable for X-ray crystal structure determination were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex (yield: 0.15 g, 52.5%). IR (pure, orbit diamond): 3310s, 2316m, 2289w, 1619m, 1571w. *Anal.* Calc. for $C_{26}H_{24}Br_2N_4NiO_2S_2$: C, 44.16; H, 3.42; N, 7.92. Found: C, 44.27; H, 3.56; N, 7.87%.

2.4. Synthesis of complex **2** [Ni(L)$_2$]

Excess of Et_3N (0.56 mL, 4.0 mmol) was added to a solution of $Ni(Br)_2(PPh_3)_2$ (0.15 g, 0.20 mmol) in THF (20 mL) until the formation of a white precipitate. (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide (0.1 g, 0.41 mmol) was added to the mixture and the solution was left under stirring overnight at room temperature. The white precipitate of $Et_3N{\cdot}HBr$ was filtered off and a yellow powder of the titled complex was obtained by solvent evaporation and then dried under vacuum. Dark monocrystals suitable for X-ray analysis were collected upon slow diffusion of diethyl ether into a THF solution of the titled complex (yield: 0.13 g, 60%). IR (pure, orbit diamond): 1648m, 1577w, 1486m, 1438m, 1367w, 1309w, 1274w, 1189s, 1120s, 1024w, 720s, 696s. *Anal.* Calc. for $C_{26}H_{22}N_4NiO_2S_2$: C, 57.27; H, 4.07; N, 10.27. Found: C, 57.25; H, 4.13; N, 10.44%.

2.5. Synthesis of complex **3** [Ni$_2$(μ-H$_2$O)(μ-L)$_2$(L)$_2$]

To a well stirred solution of (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide (0.1 g, 0.41 mmol) in THF (12.5 mL), $NiCl_2$ (0.026 g, 0.2 mmol) was added. An excess of Et_3N (0.56 mL, 4.0 mmol) was added to the solution until the formation of a white precipitate. The solution was left under stirring overnight at room temperature and then the white precipitate ($Et_3N{\cdot}HBr$) was filtered off. A green powder of the titled complex was obtained by solvent evaporation and then dried under vacuum. Green monocrystals suitable for X-ray crystal structure determination were collected by slow diffusion of diethyl ether into a dichloromethane solution of the titled complex (yield: 0.10 g, 25%). IR (pure, orbit diamond): 2363m, 1645w, 1575w, 1509m, 1423w, 1270w. *Anal.* Calc. for $C_{60}H_{62}N_8Ni_2O_7S_4$ (3·2THF): C, 57.52; H, 4.99; N, 8.94. Found: C, 57.66; H, 4.76; N, 8.87%.

2.6. Oligomerization of ethylene

4×10^{-5} mmol of Ni complex **2** was dissolved in 15 mL toluene and injected into the reactor under an ethylene flux. Then a 5 mL toluene solution of $AlEtCl_2$ (8×10^{-5} mol/L) was added to obtain a total volume of 20 mL. The reactor was pressurised to 10 bars and a rise in temperature was observed as a result of the reaction exothermicity. The 10 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of the test (35 min), a dry ice bath was used to rapidly cool down the reactor, thus stopping the reaction. An ice bath was then used and when the inner temperature reached 0 °C, the ice bath was removed allowing the temperature to slowly rise to 10 °C. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask for GC analysis. The products in the reactor were alcoholyzed *in situ* by the addition of ethanol (10 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen, in order to avoid any loss of product.

2.7. Crystal structure determinations

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. Single crystals of the ligand and complexes **1**–**3** (two different cif files are given for complex **3**, as will be explained in the text) were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα λ = 0.71073 Å). The complete conditions of data collection (DENZO software [10]) and structure refinements are given in supporting material. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 and CRYSTALBUILDER software [11,12]. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97. Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication No. CCDC 835284–835288. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336 033; e-mail: deposit@ccdc.cam.ac.uk)

3. Results and discussion

3.1. Synthesis and structural characterisation of (E)-N′-(1-(thiophen-2-yl)ethylidene)benzohydrazide (HL)

The initial task of the present work dealt with the synthesis and characterisation of (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide ligand. Following a literature procedure [13], (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide was synthesized in 4.5 min, in high yield and on a 5-g scale under microwave irradiation, starting from benzhydrazide and 2-acetylthiophene. Crystals suitable for single X-ray diffraction studies were extracted directly from this sample. The solid-state structure of (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide is depicted in Fig. 1.

The ligand H**L** crystallizes in the orthorhombic space group Pbca with eight H**L** molecules in the unit cell. In the solid state, the H**L** molecules are not planar (52° between thiophene group and phenyl ring), which contrasts with our previous observations for related ligands (i.e. quite planar in the solid state); this is probably due to the absence of an OH group on the phenyl ring [1]. Three classical intermolecular hydrogen bonds (N–H···O and C–H···O) were detected [14]. The bond lengths and angles for these interactions are as follows: N1–H1···O1*: 0.879(3)/2.463(3)/3.323(3) Å/165.8°; C1–H1A···O1*: 0.949/2.387/3.234(4) Å/148.4°; C9–H9C···O1*: 0.980/2.380/3.241(4) Å/146.3°, (* = −1/2 − *x*, −1/2 + *y*, *z*). A selected packing diagram in the (a and c) sheet is provided in Fig. 1.

3.2. Synthesis and structures of the derived Ni complexes (1–3)

3.2.1. Synthesis and crystal structure of Ni(HL)$_2$(Br)$_2$ (complex **1**)

The reaction of $NiBr_2(PPh_3)_2$ with 2 eq. of the ligand H**L** (THF, room temperature, 12 h) afforded complex **1** [$Ni(HL)_2(Br)_2$] as a green powder with reasonable yield (Scheme 2). Green crystals of complex **1** suitable for single X-ray crystal structure determination were obtained by a slow Et_2O diffusion (at room temperature) into a CH_3CN solution of pure **1**. The molecular structure of complex **1** along with a selected packing diagram is illustrated in Fig. 2.

Complex **1** crystallizes in the monoclinic space group $P2_1/c$. Its solid-state molecular structure (Fig. 2) features a Ni^{2+} metal centre located on a crystallographic inversion centre −1. The Ni^{2+} ions are surrounded by two neutral H**L** ligands and two *trans*-located bromide ligands to complete the octahedral coordination geometry (Fig. 2). The packing diagram shown in Fig. 2 also points out the position of the intermolecular N–H···Br hydrogen bonds. The parameters for intra- and inter-molecular hydrogen bonds for complex **1** are summarised in Table 1.

Our group has recently reported similar coordination modes to that observed in complex **1** with Fe^{2+} ion coordinated by closely related ligands [3,4]. To the best of our knowledge, complex **1** is the first example of transition metal complex supported by the (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide ligand. Examples of complexes featuring similar coordination modes have been reported, where the metal centres are coordinated to two *trans*-located bromides and two N^O chelating ligands [15–18].

3.2.2. Synthesis and crystal structure of **Ni(L)$_2$** (complex **2**)

When the reaction of $NiBr_2(PPh_3)_2$ with 2 eq. of the ligand HL is carried out in the presence of an excess of Et_3N (20 eq. to metal), the formation of complex **2**, in which the nickel centre is chelated by two anionic L^- ligands, is observed as deduced from X-ray crystallographic data (Scheme 3). The role of triethylamine is to capture the halide from the metal precursor, with the deposition of $Et_3N{\cdot}HBr$ (triethylamine hydrobromide) as a white solid. Dark crystals of complex **2** suitable for single crystal X-ray analysis were collected upon slow diffusion of Et_2O into a THF solution of species **2**. Fig. 3 shows the ORTEP view of complex **2** along with selected bond lengths and angles.

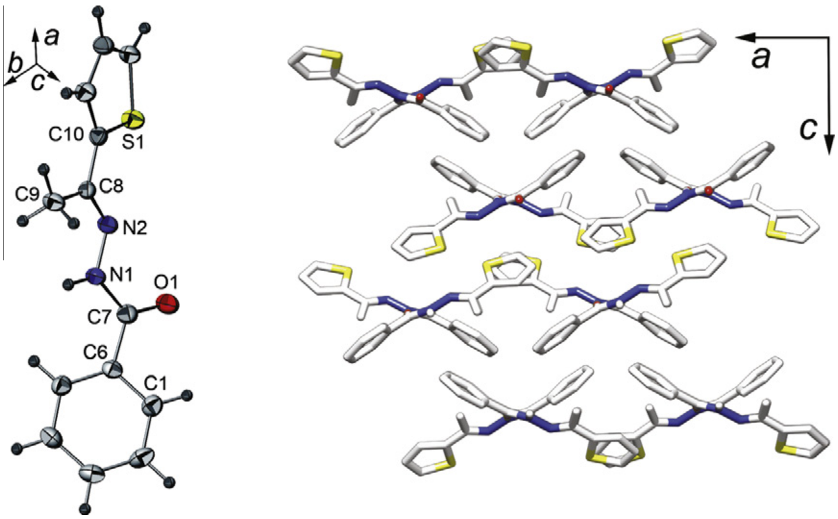
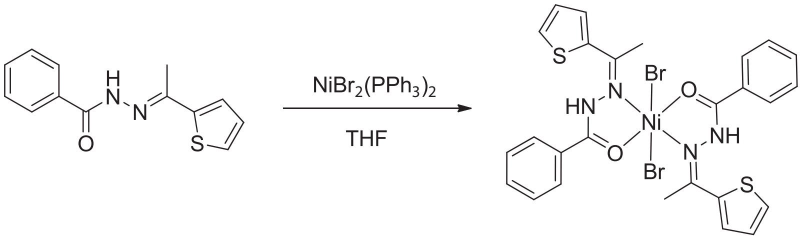


Fig. 1. ORTEP view (left) and selected packing diagram (right) of the ligand H**L** with partial labelling scheme. The ellipsoids enclose 50% of the electronic density. On the packing diagram, the H atoms have been omitted for clarity.



Scheme 2. Synthesis of Ni(HL)$_2$(Br)$_2$.

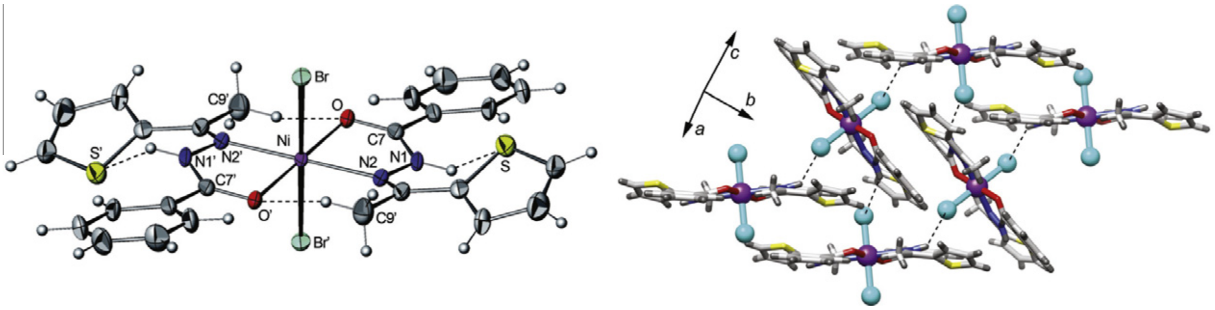
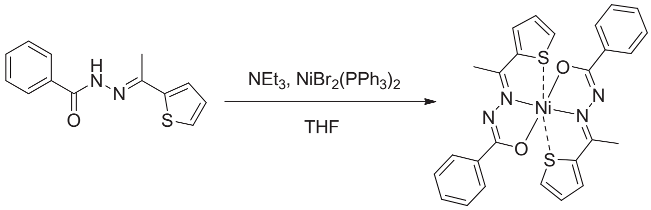


Fig. 2. Left: ORTEP view of complex **1** with a partial labelling scheme. Hydrogen bonds (intra molecular) are represented in dashed lines. The ellipsoids enclose 50% of the electronic density. Symmetry code for ′ = −*x*, −*y*, −*z*. Selected distances (Å): Br–Ni 2.5502(5), Ni–O 2.036(4), Ni–N2 2.120(5), O–C7 1.233(6), N1–C7 1.352(7), N1–N2 1.404(7). Right: packing view showing N–H···Br hydrogen bonds (dashed lines).

Table 1
Bond lengths and angles of intramolecular and intermolecular hydrogen bonds in complex **1**.

Type	Donor–H···acceptor	$d_{H–A}$ (Å)	$d_{D–A}$ (Å)	D–H–A angle (°)
Intramolecular	N(1)–H(1 N)···S	2.328	2.879(5)	120.7
Intermolecular	N(1)–H(1 N)···Br″	2.643	3.332(4)	135.9
Intramolecular	C(9)– H(9C)···O′	2.163	3.080(9)	155.1

Symmetry codes: ′ = −*x*, −*y*, −*z*; ″ = −*x*, −1/2 + *y*, 1/2 − *z*.



Scheme 3. Synthesis of Ni(L)$_2$.

Complex **2** crystallizes in a triclinic space group $P\bar{1}$ with two molecules in the unit cell. Its solid-state molecular structure exhibits a Ni^{2+} metal centre that may be seen as effectively chelated by two tridentate *N,O,S* L$_2$X-type anionic L$^-$ ligands, both of which coordinating in a *mer*-fashion. This is rather an unusual coordination mode for this type of ligand, which classically behaves as a N,O bidendate ligand. X-ray data contain no residual peak in the Fourier map differences, unambiguously indicating the absence of hydrogen on the N1 and N3 atoms and establishing the monoanionic nature of each chelating ligand (same conclusions have been made with close related ligands published by our group recently – see for examples Refs. [3–7]). In contrast to the situation in complex **1**, where the sulfur external orientation is stabilized by the N–H···S hydrogen bonding and further stabilization derives from the two extra bromide ligands, complex **2** lacks both the NH moiety and bromides due to deprotonation of the ligand by the addition of Et$_3$N. The absence of the bromide ligands together with the rotation ability of the five-member ring about the exocyclic C–C bond may facilitate the coordination of the two sulfur atoms to the nickel centre.

Yet, the Ni–S interaction appears to be rather weak, as deduced from the values of the Ni–S bond distances (2.92(1) and 2.78(1) Å for Ni–S1 and Ni–S2, respectively, in comparison with the average distance value of 2.39(2) Å founded for classical Ni–S bond – about 100 references into the CCDC data base). In a comparable example of nickel complex bearing two tridentate S^N^O ligands [19], the analogue Ni–S distances were found to be about 0.3–0.4 Å shorter than those found in complex **2**. No classical hydrogen bonds were detected in the crystal structure of complex **2** but specific CH···π interactions were observed between one hydrogen atom of the methyl group and the thiophene ring (Fig. 3, on the right). To our knowledge, species **2** constitute the first example of a Ni complex in which the Ni^{2+} metals bears two (O^N^S) tridentate ligands coordinated in *mer*-configuration. The use of complex **2** as a catalyst precursor for ethylene oligomerisation was also studied (*vide infra*).

*3.2.3. Synthesis and crystal structure of Ni$_2$(μ-H$_2$O)(μ-L)$_2$(L)$_2$ (complex **3**)*

Changing the nickel metal precursor from NiBr$_2$(PPh$_3$)$_2$ to NiCl$_2$ (under near identical reaction conditions to those used for the synthesis of species **2**) led to the formation of a new dinuclear complex **3**, whose identity and molecular structure was determined by X-ray crystallographic studies (Scheme 4, Fig. 4). The detailed reason for the formation of different complex structures by only changing the starting metal precursor is unknown at the moment. Green monocrystals of complex **3** were obtained after slow diffusion of diethyl ether into a dichloromethane solution. Suitable single crystals can also be obtained by slow diffusion of THF into dichloromethane solution of the complex. Structure determination studies were conducted for both crystalline samples (see corre-

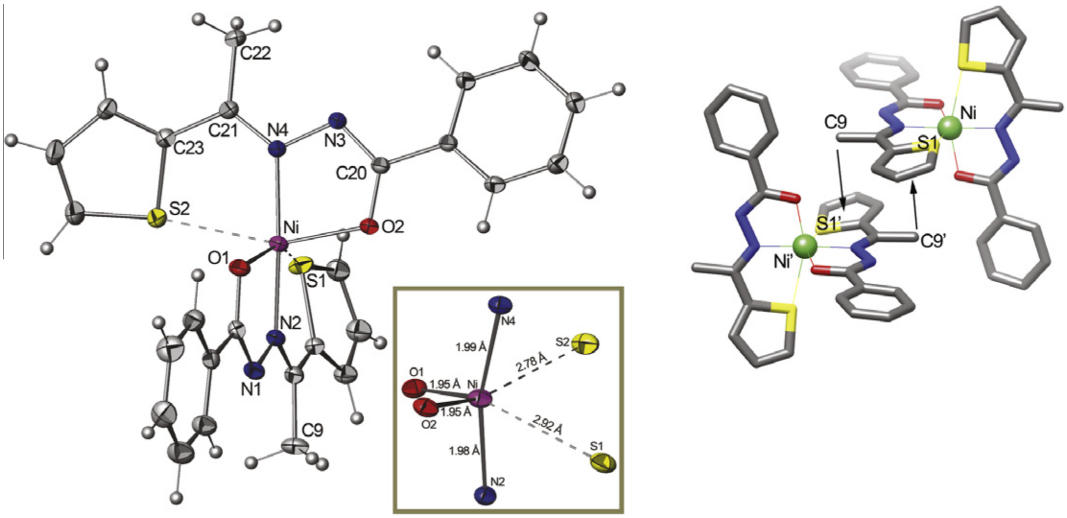
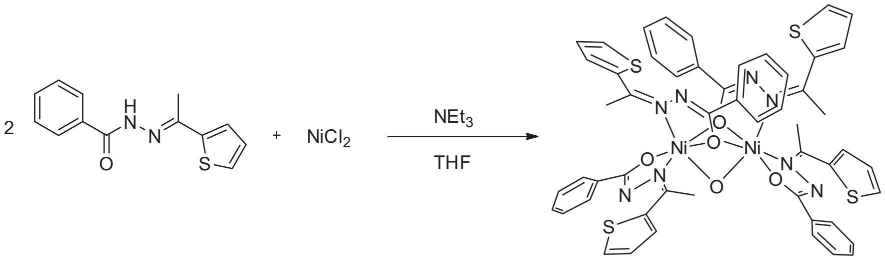


Fig. 3. Left: ORTEP view of compound **2** with partial labelling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å) and angles (°): Ni–O1 1.949(1), Ni–O2 1.949(1), Ni–N2 1.986(5), Ni–N4 1.990(1), Ni–S1 2.921(1), Ni–S2 2.781(1), O1–Ni–O2 107.85(5), N2–Ni–N4 165.58(6), O2–Ni–N4 81.27(5). Framed: selected view of the coordination sphere. Right: packing view. Arrows indicate CH⋯π bonds. Hydrogen atoms have been omitted for clarity. Symmetry code for ′ = −*x*, 1−*y*, 1 − *z*.



Scheme 4. Synthesis of $Ni_2(\mu\text{-}H_2O)(\mu\text{-}L)_2(L)_2$.

sponding cif files given in Supporting material). The crystal structure obtained by THF diffusion is the one described here.

Complex **3** crystallizes in the monoclinic space group *C*2/*c* with four molecules (each placed on the crystallographic 2-fold axis, the oxygen O3 is on the axis) in the unit cell. Complex **3** is a Ni dinuclear specie, in which the Ni metal centres are linked to one another via two bridging $\mu{:}\eta^1,\eta^2$ anionic L^- ligands and a bridging μ-O water molecule. Thus, as shown in Fig. 4, each Ni^{2+} centre is surrounded by four anionic bidendate ligands L^-: two being coordinated in a classical chelating η^2-*N,O* mode and two bridging $\mu{:}\eta^1,\eta^2$ anionic L^- moieties. Here again, the mono-anionic nature of the chelating data is supported by X-ray data: no residual peak is detected in the Fourier map differences, indicating the absence of the hydrogen atom on N1 (N1′) and N3 (N3′). The hydrogen atoms of the water molecule are also clearly detected and form two classical hydrogen bonds with the oxygen atoms of the neighbouring THF solvent molecules in the crystal packing. All these observations confirm the +2 charge of Ni. Five examples of similar coordination for Ni^{2+} dinuclear compounds can be found in the Cambridge Data base [20–24]. The Ni–Ni distance of 2.91 Å lies in the typical range for such dinuclear species. The presence of a bridging water molecule in this compound can be explained by the presence of water in the solvent used for these experiments.

3.3. Ethylene oligomerization using complex **2** as catalyst precursor

We evaluated the bis(chelate) nickel complex **2** for ethylene oligomerization catalytic activity in the presence of 10 eq. $AlEtCl_2$ as co-catalyst. Under an ethylene pressure of 10 bar, the complex **2**/$AlEtCl_2$ catalytic mixture was found to feature an activity comparable to that in related bis(chelate) Ni complexes [25,26]. Complex **2** exhibited a turnover frequency (TOF) of 31 200 mol of C_2H_4 (mol of Ni h^{-1}) in the oligomerization of ethylene with dimers (64.8% in mass) and trimers (30.7%) as the major products. Traces of C8 (3.8%) and C10 (0.7%) olefins were also detected (Fig. 5). This product distribution is in contrast to the results of the previously reported cobalt [27] and titanium [28] complexes, where the presence of thien-2-yl group in the ligand close to the metal centre usually led to the generation of olefins or polymers with longer carbon chains; this was ascribed to the coordination of the sulfur atom to the metal centre in the presumed transition state, likely to stabilize such an electron-deficient transition state for migratory insertion. The selectivity for α-olefins was relatively low (10% of 1-butene for ethylene dimers and 1.8% of α-C6 for trimers), which is probably due to the fast isomerization of the generated 1-butene and 1-hexene. Theoretical and experimental investigations reported in the literature indicate the real active site for olefin oligomerization or polymerisation to be a cationic metal alkyl species that would then allow for the binding of the monomer and its subsequent insertion [29,30]. In our case, as reported for other *N,O* bis(chelate) nickel(II) complexes with comparable ethylene oligomerization [26,31–33], it appears likely that the Lewis acid Al co-catalyst $AlEtCl_2$ abstracts one of the Ni-coordinated chelating ligand to form a reactive and electron-deficient alkyl Ni intermediate likely to be the catalytically active species [31,33].

4. Concluding remarks – summary

The (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide (H**L**), readily synthesized in high yield and on 5 g-scale within a few

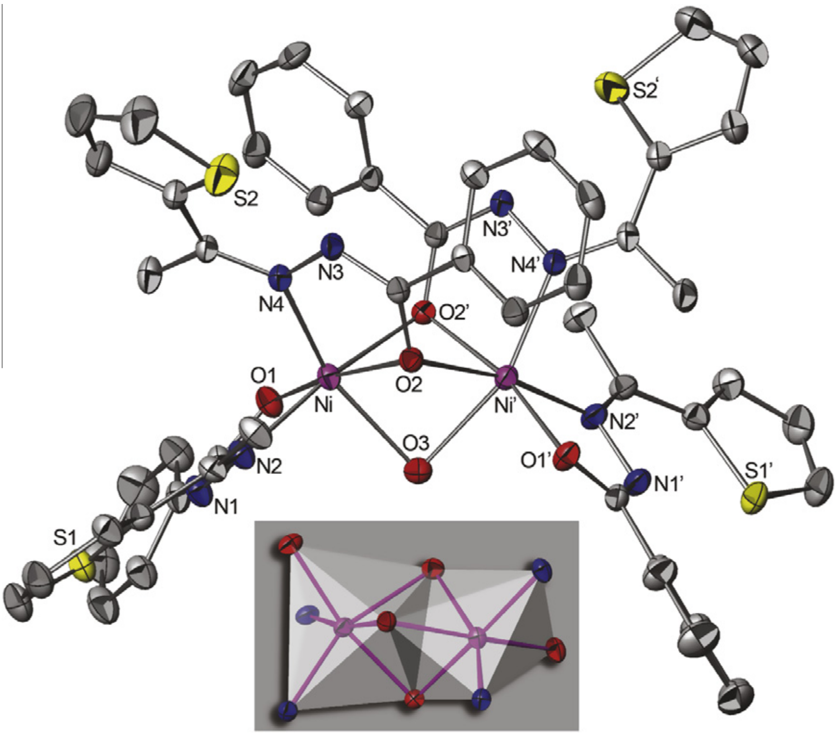


Fig. 4. ORTEP view of the complex **3** with partial labelling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å) and angles (°): Ni–O1 1.949(1), Ni–O1 2.000(2), Ni–O2 2.039(2), Ni–N2 2.053(2), Ni–N4 2.053(2), Ni–O3 2.152(2), Ni–O2 2.1570(2), Ni–Ni 2.9101(6); Ni–O2–Ni 87.78(7), Ni–O3–Ni 85.09(10). Hydrogen atoms as well as THF solvent molecules have been omitted for clarity. Symmetry code for $' = -x + 1, y, -z + 1/2$. Framed: view of the faces sharing of both deformed octahedral surrounded Ni^{2+} ions.

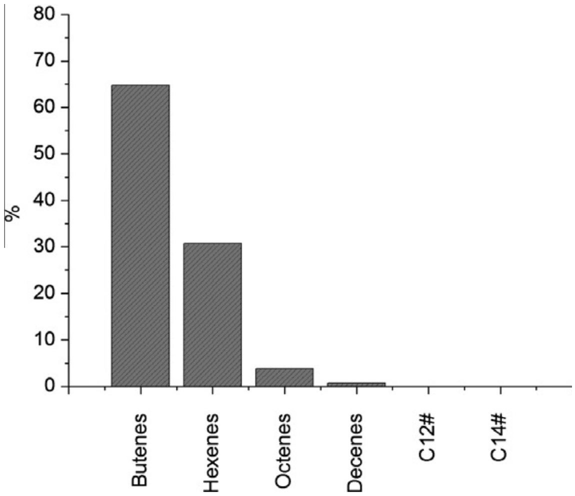


Fig. 5. Product distribution in the oligomerization of ethylene using **2**/$AlEtCl_2$ catalytic mixture.

minutes under microwave irradiation, was found to be suitable for coordination to Ni(II) and afford structurally diverse HL- and L-supported Ni derivatives. Three types of nickel complexes, $Ni(HL)_2(Br)_2$, $Ni(L)_2$ and $Ni_2(\mu\text{-}H_2O)(\mu\text{-}L)_2(L)_2$ were prepared by reaction of H**L** with different nickel sources and/or under different reaction conditions. Thus, while the reaction of $NiBr_2(PPh_3)_2$ with H**L** in the absence of base, yielded the Ni complex $Ni(HL)_2(Br)_2$ (**1**), the addition of excess Et_3N in the reaction medium led to the formation of species **2**, $Ni(L)_2$ with two unexpected and original Ni···S interactions. The dinuclear complex **3** $[Ni_2(\mu\text{-}H_2O)(\mu\text{-}L)_2(L)_2]$, in which the two Ni(II) ions are connected through two bridging $\mu{:}\eta^1,\eta^2$ anionic L^- ligands and a bridging μ-O water molecule, is accessible by the reaction of ligand HL with $NiCl_2$ in the presence of excess Et_3N. The solid-state structures of (*E*)-*N*′-(1-(thiophen-2-yl)ethylidene)benzohydrazide (H**L**) and of all three Ni complexes were all determined by single crystal X-ray diffraction studies. In the presence of 10 eq. $AlEtCl_2$ as co-catalyst, complex $Ni(L)_2$ (**2**) was found to be active in ethylene oligomerization with a TOF value of 31 200 mol of C_2H_4 $(\text{mol Ni h})^{-1}$, which is similar to those obtained with bis(chelate) Ni(II) complexes coordinated by N,O chelates [25,31,32]. C4 and C6 olefins were the main products of the latter polymerisation catalysis that occurs with low α-olefin selectivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.009.

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