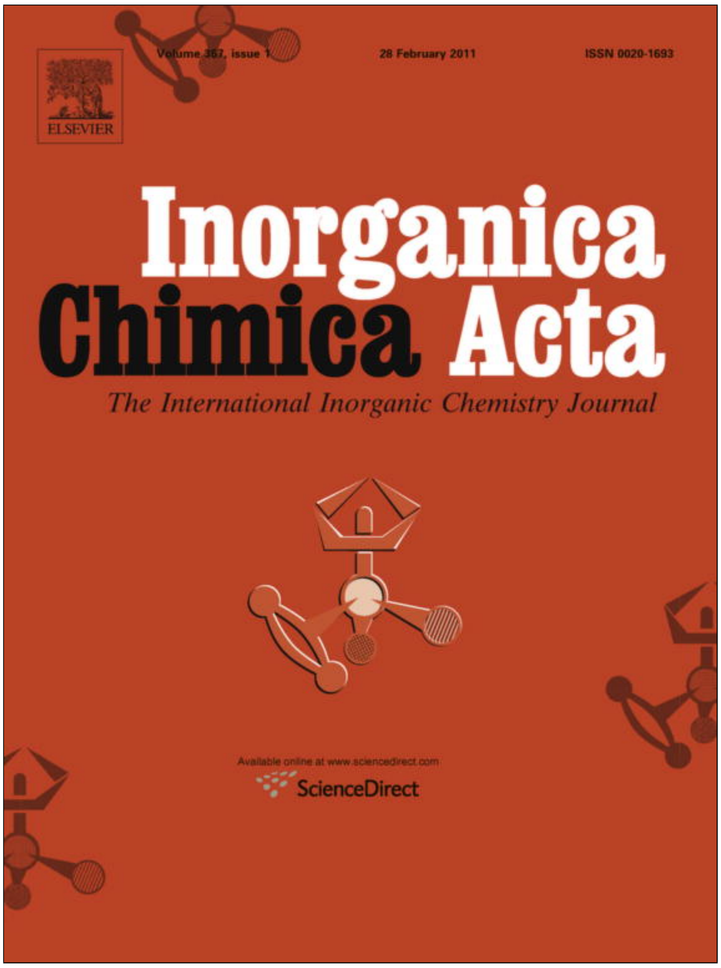
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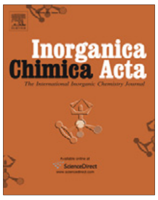

Synthesis, characterization and ethylene oligomerization studies of nickel(II) based new formazane derivatives

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ABSTRACT

A series of nickel(II) complexes based novel mono- and bis-formazan ligands has been synthesized and characterized with IR, UV, NMR spectroscopies, CHN analysis, mass spectrometry, and single crystal X-ray diffraction analysis. The prepared complexes have been tested for catalytic activity in ethylene oligomerization.

1. Introduction

Polydentate ligands based several donor centers hold an important position in modern coordination chemistry [1]. Their rational design forwards the purposeful synthesis of complexes with the prespecified coordinate bond location and the structures of forming coordination cores as well. These geometrical requirements for ligands may be met in supramolecular ensembles, such as polyligands (polymolecular associates) varying in types patterns [2].

Heterocyclic formazanes (Fig. 1), compounds containing the azo-hydrazone bond system [3], hold promise in the preparation of molecularly designed metal complex systems.

The dentation of hetarylformazanes and, consequently, structures of their metal complexes [4] are dependent on the complexing metal electron configuration, the nature and number of donor atoms in R3, R5, and their relative position in the ligand.

This work concerns the coordination behavior of the first synthesized polydentate bis-formazanes **I–VI** varied in substitutes and the conjugation pattern (Fig. 2). The presence of two formazane segments in a single molecule makes possible to synthesize mono- and binuclear metal complexes with pronounced catalytic properties.

Besides, mono-formazans **VII–X** have been synthesized as compounds of comparison to clarify the relationship between the structure and properties.

The composition of the prepared formazans has been confirmed with elemental analysis (Table 1) and mass spectrometry (Table 2).

2. Experimental

2.1. General considerations

All manipulations with air and moisture sensitive compounds were performed under an argon atmosphere using the standard Schlenk technique. Toluene was conventionally purified and distilled over 4–5 Å molecular sieves. The used ethylene was 99.9%$_{mass}$ pure. The $AlC_2H_5Cl_2$ cocatalyst in the form of a 73%$_{mass}$ petrol solution from Akzo Nobel was used with no purification.

Purity of the prepared formazanes and metal complexes was checked with TLC on fixed silica layer plates (Silufol).

Ethylene oligomerization products were analyzed with a CHROME 5 chromatograph (THERMO TR-5MS silica column, 30 m × 0.25 mm × 0.25 µm films, 5% phenyl(equiv) polysilphenylenesiloxane, $t_{col.} = 50$ °C, $T_{vap.} = 220$ °C, $T_{det.} = 220$ °C, helium flow rate 12–15 mL min^{-1}, air flow rate 100 mL min^{-1}, hydrogen flow rate 25 mL min^{-1}, sample volume ~0.02 µL).

Elemental analyses were done with a CHN PE2400SII automatic analyzer (Perkin-Elmer Insruments, USA).

Near-UV and VIS spectra were recorded with a Shimadzu UV-1800 spectrophotometer.

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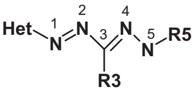


Fig. 1. Main view of formazanes ligand.

Magnetic characteristics of compounds were measured according to the Faraday's relative method at 293 K.

^{1}H NMR spectra were recorded with an AVANCE DRX-400 spectrometer (Bruker Analytik GmbH, Germany).

MS studies of formazanes and their complexes were carried out with a Shimadzu LCMS-2010 using the atmospheric pressure chemical ionization and that of electrospray with positive and negative ion detection. Samples were introduced into the spectrometer through a diode matrix SPD-M10Avp chromatographer by direct introduction into the ion source.

IR spectra were recorded in the region of 4000–400 cm^{-1} with a Shimadzu IR-AFFINITY-1 spectrometer.

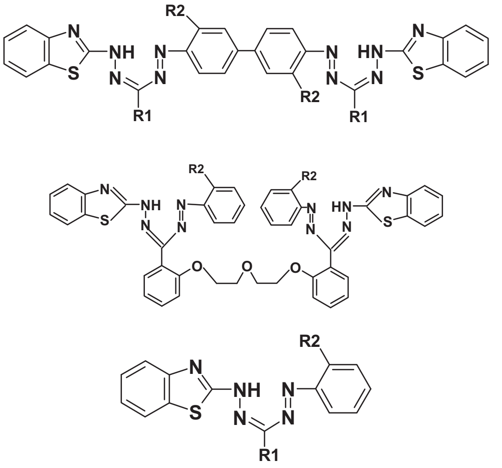
Table 2
Mass spectrometry data for formazanes and their complexes.

Compound	*m*/*z* (I, %)
I	710(32), 478(23), 446(71), 424(27)
1Ni	1442(29), 1308(23), 1172(25), 903(65), 827(31), 693(81)
III	751(32), 694(7), 482(81)
3Ni	1562(15), 1293(12), 1023(75), 783(31)
VI	873(15), 785(54), 651(66), 638(24)
6Ni	977(57), 653(81), 506(39)
VIII	396(81)
8Ni	851(65)
X	392(100)
10Ni	841(74)

2.2. Synthesis of formazanes and nickel complexes

*2.2.1. Bis-1-phenyl-3-furyl-5-(benzthiazole-2-yl)formazane (**I**)*

A diazonium salt solution, prepared from 1.31 g of benzidine (7.15 mmol) in 5 mL of concentrated HCl and 0.98 g. (14.2 mmol) of sodium nitrite in 5 mL of water, was slowly added to a cooled



I: R_1 - furyl, R_2 - H;
II: R_1-thiothenyl, R_2 - H;
III: R_1-furyl, R_2 -OCH_3;
IV: R_1- thiothenyl, R_2 - OCH_3.

V: R2-Cl;
VI: R2-OCH_3

VII : R1-furyl, R2-Cl;
VIII: R1- thiothenyl, R2-Cl;
IX: R1-pyridinyl, R2-Cl;
X: R1-thiophenyl, R2-OCH_3;

Fig. 2. The structure of synthesized formazanes.

Table 1
Characterization of benzthiazolyl formazanes and their complexes.

Compound	Yield (%)	Mp (°C)	λ_{max} (nm)	MW (g/mol)	Found (%)			Empirical formula	Calculation (%)		
					C	H	N		C	H	N
I	74	150	495	710.82	62.40	3.55	20.30	$C_{36}H_{24}N_{10}O_2S_2{\cdot}H_2O$	62.41	3.50	20.22
1Ni	75	185	680	1442.22	60.01	3.32	19.46	$C_{72}H_{46}N_{20}NiO_4S_4$	59.90	3.22	19.43
II	73	180	505	724.94	59.68	3.38	19.41	$C_{36}H_{24}N_{10}S_4$	59.64	3.34	19.33
2Ni	68	203	675	1510.87	57.14	3.15	18.71	$C_{72}H_{46}N_{20}NiS_8$	57.23	3.08	18.55
III	79	140	530	752.88	60.64	3.82	18.60	$C_{38}H_{28}N_{10}O_4S_2$	60.62	3.76	18.61
3Ni	60	179	680	1562.32	58.47	3.55	17.96	$C_{76}H_{54}N_{20}NiO_8S_4$	58.42	3.49	17.93
IV	81	160	540	785.00	58.16	3.55	17.80	$C_{38}H_{28}N_{10}O_2S_4$	58.14	3.60	17.85
4Ni	65	196	685	1626.67	56.32	3.64	17.25	$C_{76}H_{54}N_{20}NiO_4S_8$	56.11	3.52	17.22
V	68	216	440	886.01	59.72	3.40	15.81	$C_{44}H_{34}N_{10}O_3S_2Cl_2$	59.70	3.88	15.83
5Ni	42	273	555	1885.14	56.11	3.46	14.93	$C_{88}H_{64}N_{20}Ni_2O_6S_4Cl_4$	56.06	3.43	14.86
VI	51	76	400	876.96	63.70	5.31	14.52	$C_{46}H_{40}N_{10}O_5S_2{\cdot}0.5(C_7H_{15})$	64.21	5.23	15.14
6Ni	47	152	545	1867.28	59.51	4.02	15.46	$C_{92}H_{76}N_{20}Ni_2O_{10}S_4$	59.17	4.11	15.01
VII	70	198	490	381.88	56.91	3.22	18.41	$C_{18}H_{12}N_5OSCl$	56.60	3.17	18.34
7Ni	62	215	590	820.43	52.83	2.83	17.11	$C_{36}H_{22}N_{10}NiO_2S_2Cl_2$	52.70	2.71	17.08
VIII	75	193	510	397.94	54.22	3.09	17.72	$C_{18}H_{12}N_5S_2Cl$	54.26	3.04	17.69
8Ni	53	234	615	852.55	50.79	2.49	16.51	$C_{36}H_{22}N_{10}NiS_4Cl_2$	50.71	2.61	16.43
IX	69	241	505	392.94	58.23	3.40	21.45	$C_{19}H_{13}N_6SCl$	58.01	3.34	21.37
9Ni	48	256	650	842.55	54.32	3.01	20.05	$C_{38}H_{24}N_{12}NiS_2Cl_2$	54.17	2.87	19.95
X	65	150	500	393.51	57.95	3.82	17.69	$C_{19}H_{15}N_5S_2O$	57.98	3.85	17.80
10Ni	57	184	650	843.69	54.26	3.42	16.82	$C_{38}H_{28}N_{10}NiO_2S_4$	54.10	3.35	16.61

solution of 3.45 g (14.22 mmol) of 1-(benzthiazole-2-yl)-3-furylhydrazone in 50 mL of DMF. When the addition was completed, the resulted mixture was left for 20 min. Then the vigorously stirred mixture was alkalized to pH ~9 with a 2 N solution of sodium hydroxide and left for half an hour. After that a concentrated solution of acetic acid was added to reach pH about 7 and left the mixture for 10–15 h at rt. The precipitate was filtered off, washed with water, air dried, and recrystallized from acetone.

Bis-1-phenyl-3-thiophenyl-5-(benzthiazole-2-yl)formazane (**II**), bis-1-(2-methoxyphenyl)-3-furyl-5-(benzthiazole-2-yl)formazane (**III**), bis-1-(2- methoxyphenyl)-3-thiophenyl-5-(benzthiazole-2-yl) formazane (**IV**) were prepared similarly to compound **I**. Their characteristics are given in Table 1.

1,5-Bis(1′-*o*-chlorophenyl-3′-*o*-oxophenyl-5′-benzthiazolylformazyl)-3-oxopentane (**V**) was synthesized according to Ref. [5].

A diazo solution, prepared from 0.42 mL of chloroaniline in 1 mL of HCl (1:1) and 0.23 g (3.33 mmol) of sodium nitrite in 5 mL of water, was added to a cooled solution of 1.0 g (1.6 mmmol) of 1,5-bis(benzthiazolyl-2-hydrazone of salicylic aldehyde)-3-oxopentane in a mixture of 10 mL of isopropanol and 30 mL of DMF, acidified with concentrated HCl. Then the stirred mixture was alkalized to pH 8–9 with a NaOH solution and left for an hour. After that the mixture was neutralized to pH 6–7 with acetic acid. The solution was evaporated; the resulted precipitate was washed with water and dried.

1,5-Bis(1′-*o*-methoxyphenyl-3′-*o*-oxophenyl-5′-benzthiazolylformazyl)-3-oxopentane (**VI**) was prepared similarly to compound **V**.

2.2.2. 1-(2-Chlorophenyl)-3-furyl-5-(benzthiazol-2-yl)formazane (VII)

A diazonium salt solution, prepared from 0.40 g (3.1 mmol) of *o*-chloroaniline in isopropanol and 0.21 g. (3.12 mmol) of sodium nitrite in 3 mL of water, was slowly added to a stirred and cooled to ~0 °C solution of 0.75 g (3.1 mmol) of furaldehyde benzthiazolyl-2-hydrazone in 30 mL of isopropanol acidified with 2 mL of concentrated hydrochloric acid. Then the reaction mixture was alkalized to pH 8–9 with a 2 N NaOH, left for an hour, acidified to pH 7 with acetic acid, and left for 3 h at rt. The resulted brown precipitate was filtered off, washed with water, air dried, and recrystallized from acetone.

1-(2-Chlorophenyl)-3-thiophenyl-5-(benzthiazol-2-yl)formazane (**VIII**), 1-(2-chlorophenyl)-3-pyridinyl-5-(benzthiazol-2-yl) formazane (**IX**), 1-(2-methoxyphenyl)-3-thiophenyl-5-(benzthiazol-2-yl)formazane (**X**) were prepared similarly to compound **VII**.

2.2.3. Nickel(II) bis-1-phenyl-3-furyl-5-(benzthiazol-2-yl)formazanate (1Ni)

A hot water solution of 0.21 g (0.85 mmol) of $Ni(CH_3COO)_2{\cdot}4H_2O$ was added to a warmed and stirred solution of 6 g (0.85 mmol) of the formazane in 20 mL of acetone. After warming during 15 min the mixture was allowed to get cooled at rt. The precipitate was filtered off, washed with warm water, and air dried.

Nickel(II) formazanates 2Ni–10Ni were synthesized similarly to 1Ni. The characteristics of the prepared metal complexes are given in Table 1.

2.3. Crystal structure determination

Single-crystal X-ray diffraction analysis was performed at 295(2) K with an Xcalibur 3 autodiffractometric system equipped with a CCD detector. Crystals of 1-(2-methoxyphenyl)-3-thiophenyl-5-(benzthiazole-2-yl)formazan (green needles) belong to the orthorhombic system. Unit cell parameters: $a = 8.3295(5)$, $b = 20.9193(8)$, $c = 21.7123(10)$ Å, $V = 3783.3(3)$ Å^3, ρ(calc.) = 1.385 g/cm^3, $Z = 8$. The experiment completeness at $\theta < 26.38°$ was 99.4% (ω-scanning at 1° step and 20-s exposure per frame, crystal-detector distance 50 mm). To collect and edit the experimental data and refine the unit cell parameters, we used the CrysAlis CD program [6]. The structure was solved and refined using the SHELX program package [7]. The refinement was carried out by the full matrix least-squares method by F^2 with all nonhydrogen atoms taken in the anisotropic approximation. The hydrogen atoms were placed in calculated positions and included in refinement in the rider model in the isotropic approximation with dependent thermal parameters.

The formazan molecule except its benzthiazole moiety is flat; the atoms fit into the mean-square plane with a 0.1 Å deviation. The benzthiazole cycle plane is turned relative to the rest of the molecule at an angle of 6.4°. The bond lengths are typical for systems of this sort. In particular, a significant equalization of the bond lengths is observed for the formazan moiety. The molecular package is composed of oblique piles of molecules oriented along axis a. The interplanar distance between molecules inside the piles is about 3.2 Å that suggests the possibility of intermolecular π–π contacts, in particular, between the π-systems of the benzthiazole and methoxyphenyl substitutes.

The structure parameters, including atom coordinates, of 1-(2-methoxyphenyl)-3-thiophenyl-5-(benzthiazole-2-yl)formazane are registered in the Cambridge Structural Database (CCDC 764964).

2.4. General procedure for ethylene oligomerization

Ethylene oligomerization was carried out in toluene solutions in a 200 mL stainless steel jacketed reactor equipped with a magnetic stirrer, manometer, and ethylene pressure control system. The reactor jacket was supplied with thermostat-controlled water. The cleaned and inert gas washed reactor was kept evacuated for 1–2 h at 353 K. Then the reactor, heated up to a required temperature, was charged with a solvent and ethylene. Nickel formazanate and alkylaluminum dichloride, the catalyst components, were successively injected as solutions with metallic syringes from Schlenk vessels. After an hour reaction period the reactor was cooled and an excess of ethylene vented. The total volume (mass) of the products was determined and the reaction quenched by addition of 10% HCl. An aliquot of the organic phase was taken for GC analysis.

3. Results and discussion

3.1. Synthesis and characterization of nickel complexes

It was previously reported [8] that the ratios of formazane tautomers and conformers are dependent on the character of the substitutes and aggregate state. For example, according to the single-crystal X-ray diffraction data formazane **X** has the chelate $E^{1,2}Z^{2,3}Z^{3,4}$-configuration (Fig. 3), with the NH group proton located at the benzthiazole nitrogen. However, when dissolved in DMSO-d^6 both mono- (**VII–X**) and bis-formazanes **I–VI** exist substantially in the forms of disclosed tautomers as evidenced by the NH proton chemical shifts $\delta_{NH} = 8.2–9.0$ ppm [9].

FTIR spectra of 3- thiophenylformazanes **II** and **IV** show the band ν_{NH} at 3338 cm^{-1} pointing to the amine-tautomeric form of the ligand [10]. 3-Furyl-containing formazans **I** and **III** exist in the amine-imine equilibrium that supported by the bands at 3419 and 3338 cm^{-1} in their spectra.

It is known [11] that formazanes readily form complexes with nickel(II) ions. When ethanol solutions of model compounds **VII–X** (Fig. 4A) were studied using spectrophotometric titration, the resulted spectral pattern had a single isosbestic point associated

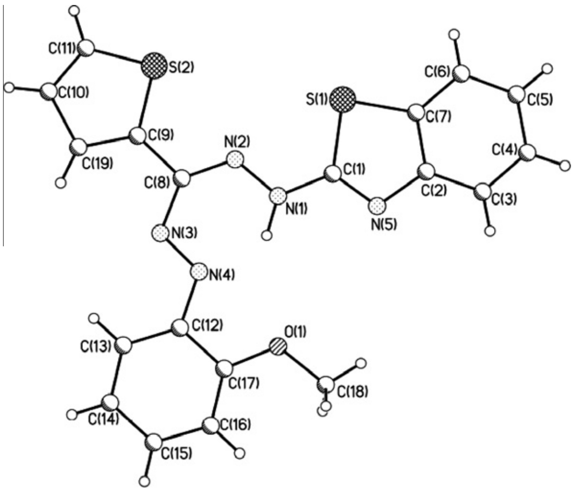


Fig. 3. Structure of 1-(2-methoxyphenyl)-3-thiophenyl-5-(benzthiazole-2-yl)formazane (**X**).

with the formation of the L_2Ni calculated composition complex. Attaching methoxy group to R2 position results in the contrast expansion of the reaction. As to a heterocyclic substitute at the *meso*-position of formazane molecule, the series furyl → thiophenyl → pyridinyl exhibits the λ_{max} bathochromic shift of 10–15 nm for the resulted complex.

Nickel formazanates 7Ni–10Ni have been isolated in a crystalline state according to Ref. [12]. For metal complexes 7Ni and 9Ni the calculated values of the magnetic moments μ_{eff} were 2.36 and 2.59 μ_B, respectively. Based on the published [13] and experimental data, the nickel formazanates were suggested to have an octahedral structure of the NiN_6 coordination core.

The electronic spectra of bis-formazanes **I–IV** demonstrate two isobestic points attesting that two types of compounds L_2Ni and L_2Ni_2 are generated sequentially. It is noteworthy that in the case of ligands **III–IV** (Fig. 4B) realization of the stoichiometric equilibrium L:Ni = 2:2 is attended by the 20–25 nm hypsochromic shift for λ_{max} of the complex.

To synthesize crystalline metal complexes the experimentally found ratio L:Ni = 2:2 was used, however the elemental analysis (Table 1) and mass spectrometry (Table 2) revealed that the prepared compounds (1Ni–4Ni) had the composition L_2Ni.

It is likely that only one formazane moiety of a bis-formazane (**I**–**IV**) ligand participates in the formation of the corresponding metal complex.

The mass-spectra contain fragment ions of 40–60% intensity from the corresponding coordination polyhedra (Table 2). According to the magnetochemical studies complex 1Ni (μ_{eff} = 2.77 μ_B) has an octahedral structure of the NiN_6 coordination core (Fig. 5A), whereas compound 3Ni with the NiN_4 formula is most likely tetrahedral (μ_{eff} = 3.23 μ_B) (Fig. 5B). In addition the structures of the 1Ni and 3Ni complexes were simulated with the HyperChem program package (HyperCube Inc., FL, USA) [14].

Compounds **V** and **VI** contain two formazane segments bound together through oxyethylene spacers. Their electronic spectra, obtained with spectrophotometric titration, demonstrate an absorption band in the 550–560 nm region from the formed complex, the reaction contrast being 100–20 nm. In solutions formazanes **V**–**VI** and nickel(II) ions form complexes of the two types: L_2Ni and L_2Ni_2 when the metal ion concentration is raised, similar to formazanes **I**–**IV**.

The elemental analysis data (Table 1) for crystalline formazanates 5Ni and 6Ni substantiate the formation of a binuclear complex L_2Ni_2. In this case two metal atoms coordinate through two donor centers of each formazane segment (Fig. 6). If the metal complex contains sufficiently flexible podand segments, the structure of binuclear metal complex 5Ni suggests that nickel atom participates in the coordination to form a tetrahedral coordination core (μ_{eff} = 3.86 μ_B).

3.2. Ethylene oligomerization

The catalytic activity of synthesized compounds 1Ni–5Ni and 7Ni–10Ni has been studied in ethylene oligomerization. Although heptane is used industrially as a medium for this reaction, we chose toluene because of its good dissolving capacity for the prepared complexes. $AlEtCl_2$ was chosen as a cocatalyst [15].

The kinetics of ethylene consumption for the nickel(II) formazanate catalytic systems is shown in Fig. 7. According to GC analysis (Table 3) the reaction products are a mixture of higher α- and β-olefins (butenes, hexenes, octenes) and alkyltoluenes (*o*-, *m*-, *p*-ethyltoluenes, di- and trisubstituted isomers of polyethyltoluenes). A high content of alkyltoluene byproducts is explained by the active Friedel–Crafts alkylation of toluene which accompanies ethylene oligomerization in higher olefins. A path toward higher yields of the target products (butenes, hexenes, octenes) can begin with a

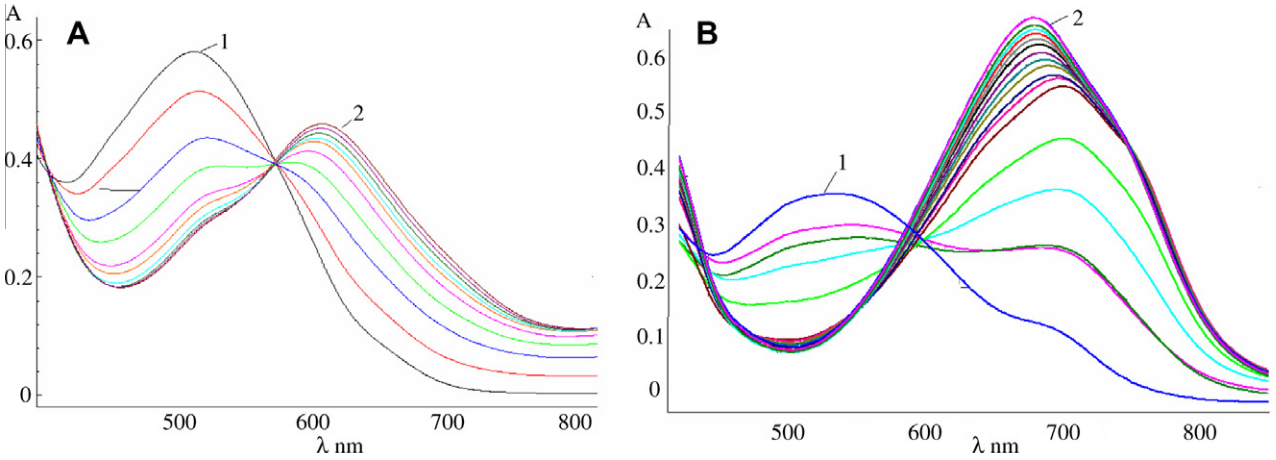


Fig. 4. Electronic spectra of formazanes **VII** (A) and **IV** (B) in acetone, recorded in the course of titration with nickel(II) acetate in water ([**VII**] = [**IV**] = 3 × 10^{-4} mol L^{-1}, $[Ni(CH_3COO)_2]$ = 0.001 mol L^{-1}). 1, initial formazane; 2, resulted metal complexes.

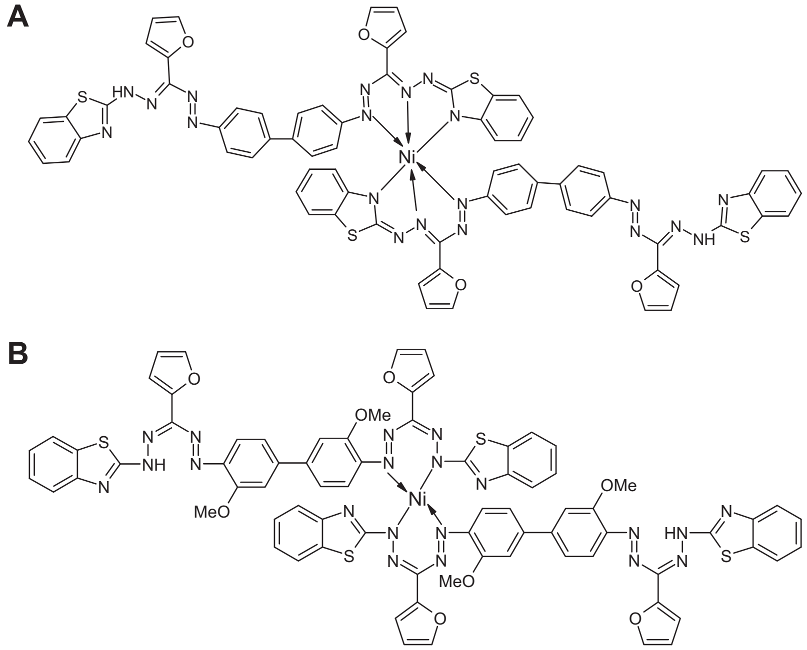


Fig. 5. Structures of complexes 1Ni(A) and 3Ni(B).

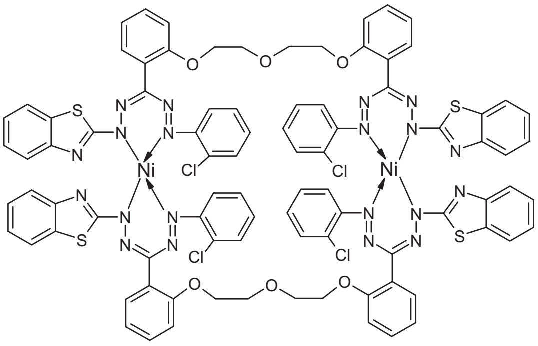


Fig. 6. Structure of binuclear complex 5Ni.

synthesis of substituted formazane ligands with a sufficient solubility in heptane.

The highest yields of the products (g/mol Ni-h) have been obtained for the nickel formazanates based on chlorine-containing mono- and bis-formazanes similarly to the reported in Ref. [16]. The presence of oxygen atoms of furyl or *ortho*-methoxyphenyl substituents in the structures of L_2Ni metal complexes essentially reduces their activity in ethylene oligomerization. As to the compounds based on bis-formazanes, complex 5Ni proved to be the most effective catalyst. Its ligands comprise two formazane moieties coupled through an oxyethylene spacer. It seemed to be the presence of binuclear nickel complexes that afforded the increased yield of the target products, according to Ref. [17].

4. Conclusion

To summarize, we have shown that nickel complexes of different composition and structure can be synthesized from bis-formazanes of a preset dentation which is governed by the nature of a coupling spacer between formazane moieties. It has been found that the synthesized complexes of nickel(II), when applied for ethylene oligomerization, proved to catalyze toluene alkylation effectively. The catalytic activity of the synthesized nickel(II) formazanate complexes depends on the nature of substitutes in the ligand and the amount of active metal centers as well.

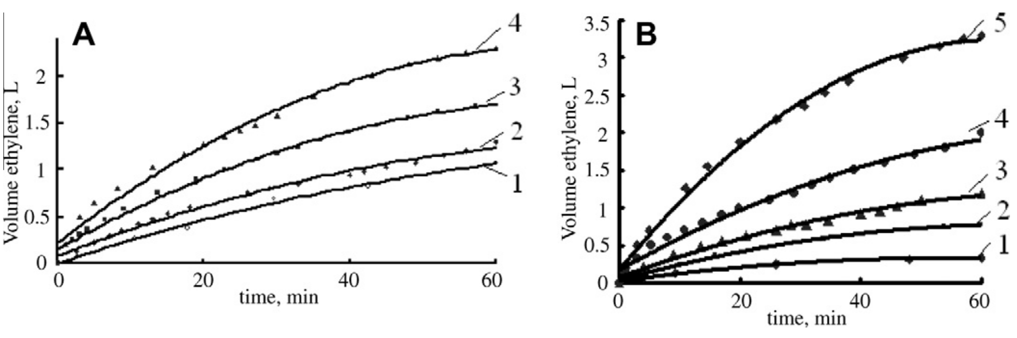


Fig. 7. Ethylene consumption *vs* reaction time for the ethylene oligomerizations catalyzed by nickel(II) formazanates in toluene ($V_{toluene}$ = 60 mL, 353 K, cocatalyst $AlC_2H_5Cl_2$, Al:Ni = 100, $C_{Ni} = 3 \times 10^{-4}$ mol L^{-1}, $P_{C_2H_4}$ = 0.4 MPa). (A) Nickel formazanate with mono-ligands: 1, **X**; 2, **VII**; 3, **VIII**; 4, **IX**; (B) nickel formazanate with bis-ligands: 1, **IV**; 2, **II**; 3, **III**; 4, **I**; 5, **V**.

Table 3
Yields and compositions of the products of ethylene oligomerization catalyzed by the systems based on nickel(II) formazanates.

Complex	Yield of the products (g/mol Ni-h)	Composition of the product mixtures (%)			
		C_4H_8	C_6H_{12}	C_8H_{16}	Products of alkylated toluene
1Ni	76.6	6	7	Traces	86
2Ni	117.5	35	54	4	7
3Ni	25.5	2	2	Traces	96
4Ni	44.3	2	2	Traces	96
5Ni	199.3	20	9	2	69
7Ni	158.4	2	5	Traces	93
8Ni	201.1	29	6	3	62
9Ni	270.9	26	7	3	64
10Ni	155.1	22	8	4	66

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.11.044.

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