# Catalytic Activity of New Nickel(II) Formazanates in Ethylene Oligomerization

A. V. Zaidman<sup>a</sup>, I. I. Khasbiullin<sup>b</sup>, G. P. Belov<sup>c</sup>, I. G. Pervova<sup>a</sup>, and I. N. Lipunov<sup>a</sup>

<sup>a</sup>Ural State Forest Engineering University, Yekaterinburg, Russia e-mail: Zaidman@yandex.ru

<sup>b</sup>Kazan State Technological University, Kazan, Russia

e-mail: khailnaz@yandex.ru

<sup>c</sup>Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia

e-mail: gbelov@cat.icp.ac.ru Received May 12, 2011

Abstract—Thirteen mono- and three bisformazans containing one system of azahydrazone bonds have been synthesized, as well as mono- and binuclear complexes on their basis. The kinetic features of ethylene oligomerization in the presence of catalytic systems on the basis of  $AlEtCl_2$ -activated Ni(II) formazanates differing in composition and structure have been studied. The structures of the mono- and binuclear complexes differ by substituents in the formazan ligand, which have an effect on the activity of the systems and the product composition. The catalytic activity of the binuclear complexes is several times below that of mononuclear Ni(II) formazanates.

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Creation of new high-performance catalytic systems for oligomerization of  $\alpha$ -olefins remains an important task, since the demand for new oligomeric materials does not pass and the progress in controlling the structure and properties of oligomers was always associated with the development of catalysts with new structure [1]. Metal complexes of Ni(II) with "nitrogen-skeleton" organic ligands in combination with organoaluminum compounds showed themselves to advantage as such catalytic systems [2].

Formazans (azahydrazones) [3], polydentate chelate ligands, have already been known in many areas of practical application including catalysis. Wide variability of substituents in formazan molecules and relative ease of their synthesis make it possible to study the influence of the fine ligand structure on the catalytic activity of metal complexes in ethylene oligomerization.

Earlier [4] we have studied the influence of location of chlorine-containing substituents in formazan ligands, temperature, pressure, and Al/Ni molar ratio on the reaction kinetics and the product composition of ethylene oligomerization in the presence of a catalytic system based on Ni(II) formazanates and EtAlCl<sub>2</sub>. It was shown that effective metal complex systems can be obtained by varying the ligand composition and structure.

This study is in continuation of our investigation into the influence of the nature of substituents in the structure of Ni(II) formazanates on their catalytic activity in ethylene oligomerization. In addition, we report in this paper data on the influence of the composition of the inner coordination sphere and the number of active metal centers on the catalytic activity of these complexes in the ethylene oligomerization reaction.

# **EXPERIMENTAL**

### Ethylene Oligomerization

The reaction was carried out in toluene for 1 h in a stainless steel reactor of 0.2 l volume equipped with a magnetic stirrer and a gauge for controlling the ethylene pressure. The cleaned, inert gas-purged reactor was evacuated for 1–2 h at 353 K. A calculated amount of solvent and ethylene were fed to the reactor heated to a desired temperature, and then solutions of the catalyst components Ni(II) formazanate and ethylaluminum dichloride were successively injected with a metal syringe (Schlenk technique). Toluene was preliminary purified according to the standard procedure by distillation over 4–5 Å molecular sieves. Ethylene was of 99.9 wt % purity. The cocatalyst AlC<sub>2</sub>H<sub>5</sub>Cl<sub>2</sub>, taken as a 73 wt % solution in benzene, was not additionally purified.

# Product Analysis

The products were determined chromatographically on a Chrom-5 chromatograph: a TR-5 MS capillary column (manufactured by Thermo Fisher Scientific) of 30 m  $\emptyset$  0.25 mm in size with 5% phe-

nylpolysylphenylene–siloxane inner film of 0.25  $\mu$ m thickness; the carrier gas was argon, with a flame-ionization detector. The elemental analysis was carried out on a Perkin-Elmer PE2400SII automated CHN analyzer. The proceeding of the reaction was monitored and synthesized Ni(II) complexes were identified by TLC on Silufol-254 plates (acetone : hexane = 1 : 1 blend as an eluent). Electronic absorption spectra in the visible and near-UV regions were recorded on a Shimadzu UV-2100 spectrophotometer. The magnetic characteristics were measured by the relative Faraday technique at temperatures in the range of 288–293 K [5] at the Institute of Solid State Physics, Ural Branch, Russian Academy of Sciences (Yekaterinburg).

#### Synthesis of Ligands and Metal Complexes

Synthesis of monoformazan 1. A diazonium salt solution prepared from 2.30 g of p-chloroaniline (18.04 mmol) dissolved in 5 ml of concentrated HCl and 1.24 g (18.04 mmol) of sodium nitrite in 5 ml of water was slowly added to a solution of 3.45 g (18.04 mmol) of the corresponding hydrazone in 50 ml of DMF. After the addition of the whole amount of the diazosolution, the resulting mixture was held for additional 20 min. then a 2 N NaOH solution was added with vigorous stirring until  $pH \sim 9$ , and the mixture was left to stay for 30 min. A concentrated acetic acid solution was added to the resultant mixture to have  $pH \sim 7$ , and the mixture was held at room temperature for 10–15 h. The precipitate was filtered off, washed with water, dried in air, and recrystallized from acetone. Formazans 2-13 were synthesized according to the same procedure.

Synthesis of formazan 16. A diazonium salt solution prepared from 0.31 g of bisaminobissulfide (1.12 mmol) dissolved in 5 ml of concentrated HCl and 0.15 g (2.2 mmol) of sodium nitrite in 5 ml of water was slowly added to a solution 0.53 g (2.2 mmol) of 1-(benzothiazol-2-yl)-3-pyridinylhydrazone in 25 ml of isopropanol. After the addition of the diazosolution, the resulting mixture was held for additional 20 min in an ultrasonic bath, a 2 N NaOH solution was added with vigorous stirring until pH  $\sim$  10, and the mixture was left to stay for 40 min. A concentrated hydrochloric acid solution was added to the resultant mixture to pH  $\sim$  7, and the solution was held at room temperature for 2-3 h. The precipitate was filtered off, washed with water, dried in air, and recrystallized from ethanol.

Formazans 14 and 15 were synthesized according to the same procedure.

Synthesis of metal complex I was conducted as described in [6]. A solution of Ni(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O (0.85 mmol) in 10 ml of water was added dropwise with continuous stirring to a solution of formazan 1 (0.85 ml) in 50 ml of acetone at  $40 \pm 5^{\circ}$ C. The resulting mixture was stirred for 30 min and then evaporated to 15 ml. The precipitate was filtered off, washed successively with warm distilled water and isopropanol, and dried in air.

Complexes **II**–**XVI** were synthesized according to the same procedure.

# **RESULTS AND DISCUSSION**

Monoformazans 1-10 containing one system of azahydrazone bonds and mononuclear complexes on their basis (I-X) were synthesized according to scheme 1:



Scheme 1. Synthesis of formazans and their complexes.

The substituents in the synthesized compounds is specified in Table 1. Table 2 gives the main characteristics of the synthesized formazans and Ni(II) complexes on their basis.

According to X-ray analysis data for a variety of mononuclear Ni(II) complexes with formazan

ligands [7], the coordination unit  $NiN_6$  has the octahedral form, which can be noticeably distorted by substituents on the phenyl ring at N1 according to [8]. Therefore, in was assumed that metal complexes I-X have the same structure of the coordination unit.

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Formazan no.	R1	R2	R3	R4	R5	Metal complex no.
1	CH <sub>3</sub>	Н	Н	Cl	Н	Ι
2	$C_6H_5$	Cl	Н	Н	Н	II
3	$CH_3$	Cl	Н	Cl	Η	III
4	$C_6H_4$ -4-OCH <sub>3</sub>	Cl	Н	Н	Cl	IV
5	$C_2H_5$	Br	Н	Н	Н	V
6	$C_7H_{15}$	Н	Н	Br	Н	VI
7	CH <sub>2</sub> Br	Н	Н	Н	Н	VII
8	$C_6H_4$ -4-OCH <sub>3</sub>	Н	F	F	Н	VIII
9	$C_3H_7$	Н	F	F	Н	IX
10	C <sub>6</sub> H <sub>3</sub> -2-OH-5-Br	Н	F	F	Н	X
11	$CH(CH_3)_2$	OH	Н	Н	$NO_2$	XI
12	$C_4H_9$	OH	Н	NO <sub>2</sub>	Н	XII
13	$CH_3$	OH	Н	Н	SO <sub>3</sub> H	XIII
14	$C_6H_5(n=1)$	Н	Н	Н	Н	XIV
15	$C_6H_5 (n=2)$	Н	Н	Н	Н	XV
16	$C_5H_4N\ (n=1)$	Н	Н	Н	Н	XVI

**Table 1.** Structure of synthesized formazan ligands

All metal complexes synthesized in this work were tested for catalytic activity in ethylene oligomerization. According to GC data (Table 3) the products form a mixture consisting of higher olefins. The amount of  $\alpha$ -olefins, butane-1 and hexane-1, in the mixture is 30–50%.

Among Ni(II) metal complexes I–IV, compounds III and I synthesized from chlorosubstituted formazans containing the methyl group at the C3 atom exhibit a high catalytic activity. Among all chlorophenyl-containing Ni(II) formazanates, compound III in which chlorine atoms simultaneously present in the *ortho-* and *para*-positions on the phenyl ring at N1 (Fig. 1a) has the highest activity. In the case of metal complexes I and II synthesized from mono-chlorosubstituted formazans, it is difficult to determine what factor has a greater effect on the change in activity: stereoposition of chlorine substituent in the phenyl moiety or a change in geometric size of the peripheral substituents in the C3 position. In the previous paper [4], we noted that the presence of a relatively small alkyl substituent in the C3 position of the formazan ligand is preferred to the presence of a bulky aryl moiety. Thus, the activity of formazanate II (phenyl substituent at C3) is 25% lower in comparison with complex I and the catalytic activity of metal chelate IV containing the bulky *p*-methoxyphenyl substituent in the C3 position of the formazan chain decreases by more than a factor of 4 compared with complex III.

At the same time, it was noted that it is the presence of substituents in the aryl moiety at N1 for brominecontaining complexes V–VII that plays the determining role in the change in catalyst activity (Fig. 2a). For example, the substitution of bromine into the C3 position of VII decreases the activity by a factor of 2–4 as compared with bromophenyl-substituted com-



Fig. 1. Ethylene consumption rate curves during oligomerization in the presence of catalytic systems based on Ni(II) formazanates (a) I–IV and (b) VIII–X.

# CATALYTIC ACTIVITY OF NEW NICKEL(II) FORMAZANATES

No.	M <sub>p</sub> , °C	Found, %		, )			Calculated, %		
		С	Н	Ν	Empirical formula	Mw, g/mol	С	Н	Ν
1	174	54.74	3.68	21.20	C <sub>15</sub> H <sub>12</sub> N <sub>5</sub> ClS	329.81	54.63	3.67	21.23
Ι	195	50.31	3.15	19.67	$C_{30}H_{22}N_{10}NiCl_2S_2$	716.44	50.29	3.10	19.56
2	212	61.42	3.65	17.96	$C_{20}H_{14}N_5ClS$	391.89	61.30	3.60	17.87
II	263	57.30	3.32	16.80	$C_{40}H_{26}N_{10}NiCl_2S_2$	840.46	57.16	3.12	16.67
3	156	49.40	3.06	19.20	$C_{15}H_{11}N_5Cl_2S$	364.26	49.46	3.04	19.23
III	205	45.92	2.69	17.90	$C_{30}H_{20}N_{10}NiCl_{4}S_{2} \\$	785.20	45.89	2.57	17.84
4	183	55.34	3.36	15.48	$C_{21}H_{15}N_5Cl_2SO$	456.36	55.27	3.31	15.35
IV	208	52.12	2.98	14.63	$C_{42}H_{28}N_{10}NiCl_{4}S_{2}O_{2} \\$	969.40	52.03	2.92	14.45
5	197	49.50	3.68	18.50	$C_{16}H_{14}N_5BrS$	388.29	49.49	3.63	18.04
V	231	46.23	3.21	16.87	$C_{32}H_{26}N_{10}NiBr_2S_2$	833.26	46.12	3.15	16.81
6	182	55.72	5.31	15.40	$\mathrm{C}_{21}\mathrm{H}_{24}\mathrm{N}_{5}\mathrm{BrS}$	458.43	55.02	5.28	15.28
VI	238	52.01	4.86	14.55	$C_{42}H_{46}N_{10}NiBr_{2}S_{2} \\$	973.54	51.81	4.77	14.39
7	208	48.20	3.31	18.84	$C_{15}H_{12}N_5BrS$	374.26	48.14	3.23	18.71
VII	250	44.87	2.89	17.60	$C_{30}H_{22}N_{10}NiBr_2S_2$	805.20	44.75	2.76	17.40
8	143	59.63	3.68	16.70	$C_{21}H_{15}N_5F_2SO$	423.45	59.57	3.57	16.54
VIII	186	55.86	3.21	15.64	$C_{42}H_{28}N_{10}NiF_{4}S_{2}O_{2} \\$	903.58	55.82	3.13	15.50
9	157	56.80	4.23	19.57	$C_{17}H_{15}N_5F_2S$	359.40	56.81	4.21	19.49
IX	205	52.70	3.78	18.22	$C_{34}H_{28}N_{10}NiF_{4}S_{2} \\$	775.48	52.66	3.65	18.07
10	168	49.31	2.56	14.59	$C_{20}H_{12}N_5BrF_2SO$	488.32	49.19	2.48	14.34
Х	224	45.80	2.50	14.05	$C_{40}H_{22}N_{10}NiBr_2F_4S_2O_2$	1033.32	45.49	2.15	13.56
11	190	53.21	4.36	21.97	$C_{17}H_{16}N_6SO_3$	384.42	53.12	4.20	21.86
XI	201	46.55	3.39	19.28	$\mathrm{C}_{17}\mathrm{H}_{14}\mathrm{N}_{6}\mathrm{NiSO}_{3}$	441.13	46.28	3.21	19.06
12	184	54.43	4.72	21.23	$C_{18}H_{18}N_6SO_3$	398.45	54.26	4.55	21.09
XII	219	47.60	3.74	18.68	$C_{18}H_{16}N_6NiSO_3$	455.16	47.50	3.55	18.46
13	175	46.12	3.40	17.82	$C_{15}H_{13}N_5S_2O_4$	391.43	46.03	3.35	17.89
XIII	196	40.55	2.68	15.50	$\mathrm{C}_{15}\mathrm{H}_{11}\mathrm{N}_{5}\mathrm{Ni}\mathrm{S}_{2}\mathrm{O}_{4}$	448.11	40.20	2.48	15.63
14	232	62.71	4.32	17.56	$C_{42}H_{32}N_{10}S_4$	804.98	62.66	4.02	17.40
XIV	240	59.14	4.02	16.70	$C_{84}H_{60}N_{20}Ni_2S_8$	1723.52	58.52	3.52	16.25
15	215	63.26	4.25	17.21	$C_{43}H_{34}N_{10}S_4$	819.01	63.06	4.19	17.11
XV	244	59.60	3.96	16.52	$C_{86}H_{64}N_{20}Ni_2S_8$	1751.58	58.95	3.68	16.00
16	180	59.65	3.78	20.92	$C_{40}H_{30}N_{12}S_4$	806.97	59.53	3.75	20.83
XVI	246	55.97	3.61	19.80	$C_{80}H_{56}N_{24}Ni_2S_8$	1727.48	55.61	3.27	19.46

**Table 2.** Characterization of benzothiazolylformazans and their Ni(II) complexes

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**Table 3.** Catalytic activity of Ni(II) formazanates in ethylene oligomerization reaction ( $V_{\text{reac.mix}} = 60 \text{ ml}$ ;  $T = 80^{\circ}\text{C}$ , cocatalyst, AlC<sub>2</sub>H<sub>5</sub>Cl<sub>2</sub>;  $p_{\text{ethylene}} = 0.4 \text{ MPa}$ ;  $C_{\text{Ni}} = 3 \times 10^{-4} \text{ mol/l}$ , AlC<sub>2</sub>H<sub>5</sub>Cl<sub>2</sub> : nickel chelate molar ratio = 100 : 1; solvent, *n*-heptane)

Metal complex no	$\mathbf{I} \cdot \mathbf{M}$	Activity, $kg/(g_{Ni} h)$	Olefin composition, wt %			
wietai complex no.			$\Sigma C_4 (C_4 - 1)$	$\Sigma C_6(C_4-1)$	$\Sigma C_8$	
Ι	L <sub>2</sub> Ni	21.1	73 (41)	11.3 (44)	15.7	
II	$L_2Ni$	16.5	88.4 (48)	10.6 (35)	1	
III	$L_2Ni$	26.5	39.6 (36)	58.3 (49)	2.1	
IV	L <sub>2</sub> Ni	7.3	60 (40)	37 (51)	3	
V	$L_2Ni$	11.0	27.5 (31)	31.3 (42)	41.3	
VI	$L_2Ni$	23.8	55.8 (52)	25.6 (54)	18.6	
VII	$L_2Ni$	5.5	16 (38)	12 (41)	72	
VIII	$L_2Ni$	7.4	27 (31)	23 (34)	50	
IX	L <sub>2</sub> Ni	33.8	39.4 (48)	55.2 (31)	5.4	
Χ	L <sub>2</sub> Ni	8.2	15 (41)	14 (28)	71	
XI	LNi	11.1	12 (35)	16 (34)	72	
XII	LNi	5.5	14 (43)	23 (34)	63	
XIII	LNi	4.6	21 (30)	32 (39)	47	
XIV	$L_2Ni_2$	8.2	25 (24)	31 (30)	46	
XV	$L_2Ni_2$	7.4	19 (21)	28 (25)	53	
XVI	$L_2Ni_2$	9.2	14 (32)	30 (31)	46	

plexes V–VI (Table 3). The greatest activity in this reaction catalyzed by fluorosubstituted complexes VIII–X was displayed by compound IX. This is believed [9] to be due to the electron-donating effect of fluorine-containing substituents, which increase the electrophilicity of the nickel center thus, in turn, decreasing the activation energy of ethylene insertion. However, the introduction of rather bulky *p*-methoxyphenyl substituent in the C3 position of fluorine-containing ligand (VIII), as in the case of chlorine-containing complex IV, results in a sharp decrease in activity of the catalytic system. A similar influence of peripheral substituents on the activity and molecular weight (MW) of product polyethylenes (PE) was noted by Ivancheva et al. [10], who used phenoxyimine complexes of titanium as an example to show that replacement of the methyl substituent in the *para*-position of the phenoxy group by the *tert*-butyl radical decreases the activity by a factor of 2.5. But even in this case, the cited authors admit the existence of the optimal volume of substituents above which their stimulating influence on the activity of the catalytic system decreases or is absent at all. Figure 1b depicts the obtained kinetic curves of ethylene oligomerization in the presence of metal complexes **VIII–X**.

The presence of fluorine atoms in the phenyl substituent at N1 along with the 2-hydroxy-5-bromophe-



Fig. 2. Ethylene consumption rate curves during oligomerization in the presence of catalytic systems based on Ni(II) formazanates (a) V–VII and (b) XI–XIII.

nyl substituent in the C3 position facilitates an increase in activity of the catalytic system based on metal complex X as compared with VII. It may be assumed that the stereoposition of substituents on the phenyl group at N1 of the formazan chain plays a significant role in varying the activity of the complex in comparison with the steric volume of substituents in the C3 position.

As it was stated previously [3] the introduction of hydroxyl group in the *ortho*-position of the phenyl substituent of ligands 11-13 favors the formation of mononuclear LNi complexes **XI**-**XIII** with the NiN<sub>3</sub>O coordination unit.



Judging from the structure of metal complexes, it might be expected that they would exhibit a high catalytic activity due to easy accessibility of the metal site to substrate. However, the results of the experiments showed that most mononuclear Ni(II) formazanate complexes exhibited the lowest activity (Fig. 2b). This fact is consistent with published data [11] on structurally close Ni(II) complexes with unsymmetrical electronically flexible ligands based on N-(o-phenoxyphenyl)pyridaldimine derivatives. The catalytic activity of these complexes in ethylene oligomerization at MAO activation in toluene was found to be very low or absent altogether.

It is known [12] that compounds with different amounts of active metal sites can be highly efficient catalysts in ethylene oligomerization. The denticity of formazan ligands makes it possible to synthesize biand polynuclear complexes having higher activity in this reaction. The interest in binuclear complexes based on novel bisformazans is also due to the fact that besides the properties inherent in mononuclear complexes they can exhibit unique catalytic behavior due to the presence of several active centers. According to [13], it is expected that binuclear complexes are more active as the greater steric loading of the molecule must more effectively prevent the contacts of active centers with each other. The use of binuclear complexes for oligomerization makes it possible to obtain absolutely new polymeric materials (that cannot be obtained on mononuclear analogues) owing to the cooperative effect of different active centers [14], which is observed only in the case of olefin polymerization on binuclear metallocenes [15].

Bisligands 14–16 and binuclear Ni(II) complexes on their basis (**XIV**–**XVI**) were synthesized according to the scheme 2:



Scheme 2.



**Fig. 3.** Ethylene consumption rate curves during oligomerization in the presence of catalytic systems based on Ni(II) formazanates **XIV–XVI**.

Complexing with metal ions, bisformazans 14–16 containing sulfur-ethylene spacers are capable of multi-variant geometric conformations due to the structural nature of the spacers. According to elemental analysis and mass-spectrometric data, **XIV**-**XVI** are binuclear  $L_2Ni_2$  complexes. The formation of such complexes is possible if two chelating formazan groups from each of the two bisligand molecules coordinate to the nickel atom .

Testing the catalytic activity of binuclear Ni(II) complexes **XIV**–**XVI** (Fig. 3) has revealed that they rank several times below mononuclear Ni(II) formazans in activity.

However, the first steps on synthesis of binuclear Ni(II) complexes from bisformazans demonstrated both the feasibility of preparation of such compounds and their catalytic activity in ethylene oligomerization. In particular, using as an example binuclear Ti complexes based on tetradentate salicylaldimine ligands with different aryl-containing spacers between the imine groups, Ivancheva et al. [16] demonstrated that the catalytic activity of the complexes can be varied depending the nature of the spacer in the ligands. Therefore, in our case, in order to formulate the requirements for the structure of binuclear Ni(II) formazanates exhibiting a high catalytic activity in ethylene oligomerization, it is necessary to synthesize and examine complexes with a wide variety of bisformazans differing in the nature of the bridge between formazan groups.

In summary, the nature of substituents in the phenyl moiety at N1 of the formazan ligand has a considerable

influence on the activity of the catalytic complex and the product composition. The steric volume of peripheral substituents in the C3 position can alter the catalytic activity of the system. In order to produce highly efficient catalysts on the basis of binuclear complexes containing bisformazan ligands, it is necessary to continue studies on the synthesis of ligands with different modes of conjugation of the formazan fragments in the molecule and to subsequently examine their complexes in the ethylene oligomerization reaction.

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