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Inorganica Chimica Acta xxx (2013) xxx-xxx

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

Coordination compounds of chromium (+3) and vanadium (+3) and (+5) with 2,6-bis(diphenylhydroxymethyl)pyridyl ligand: Synthesis and study of catalytic activity in the polymerization of ethylene

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ARTICLE INFO

Article history: Received 8 July 2012 Received in revised form 1 November 2012 Accepted 3 November 2012 Available online xxxx

Keywords: Olefin polymerization Vanadium Chromium Tridentate ligands X-ray structure

1. Introduction

The vast majority of post-metallocene catalysts of olefin polymerization are coordination compounds of titanium, zirconium [1,2], iron, cobalt, or nickel [3,4]. Very little is known of the catalytic activity of vanadium and chromium derivatives for this reaction, but overall properties of such complexes deem to be very promising [5–17]. The interest in studying these complexes stems from their overall similarities to the coordination compounds of group IV metals. Indeed, the compounds of vanadium (III) are isoelectronic analogs of Ti, Zr, and Hf (IV) compounds which show the highest activity in polymerization. Although activity of vanadium catalysts is generally found to be lower than that of other systems, their major advantage is in their ability to form high- and ultrahigh-molecular-weight polymers, as well as copolymers of ethylene with α -olefins containing high amounts of the comonomer.

Application of currently available organoaluminum compounds as activators of vanadium-containing catalysts is yet another area worth investigating.

Chromium complexes demonstrate weak catalytic activity in common polymerization reactions; however they have a notable

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ABSTRACT

Coordination compounds of chromium (III) and vanadium (III) and (V) with 2,6-bis(diphenylhydroxymethyl)pyridine have been synthesized. Composition and properties of the obtained complexes have been evaluated by NMR, IR spectroscopy, X-ray diffraction, and elemental analysis. Depending on the nature of the metal and the synthesis conditions, there are various types of coordination state of the terdentate pyridine ligand in the obtained complexes: it can bind either as a dianionic, bisalkoxide, terdentate (compounds **5**, **7**, **8**, **9**), monoanionic, alkoxide/alkohol, terdentate (compounds **4**, **6**) or as a neutral, bisalkohol, terdentate ligand (compound **3**). Coordination compounds of chromium were found to be incapable of catalytic polymerization of ethylene. Catalytic activity of vanadium (III) and (V) complexes in this reaction varied between 85 and 578 kg PE/mol V h after activation with diethylaluminum chloride, depending on the V/Al ratio.

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activity in the di-, tri- and oligomerization of olefins [16]. Such their property makes it possible to use chromium complexes as a component of the tandem catalytic systems used in synthesis of elastomers.

Most works evaluating polyolefin synthesis used phenoxyimine [12,17] and 2,6-bis(imino)pyridyl [3] ligands, while systems with oxygen chelating ligands have been studied to much lesser extent [18–22].

One of the problems encountered when studying the vanadium-containing catalysts is that the metal easily converted to lower oxidation states; as a consequence, the catalytic activity may decline or disappear [8,23–27]. Nevertheless, it may be reasonably expected that the type of ligand environment, the number, size, and electronic properties of both a ligand and a central atom will affect not only the catalytic characteristics of the complexes but also their ability to withstand metal reduction.

In this study we use a ligand **1** combining pyridine core and two diphenylcarbinol fragments. Ligand **1** has very limited use in coordination chemistry. It have been used to prepare complexes of hypervalent pentacoordinated dimethyltin (IV) [28], germylenes and stannylenes [29], different titanium complexes [30]. Only in our previous work [31] complexes of titanium and zirconium-based on ligand **1** have been proposed as catalysts for olefin polymerization.

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In this study we report synthesis of a new group of chromium (III) as well as vanadium (III) and (V) coordination compounds based on ligand **1**; and the investigation of their catalytic properties in polymerization of ethylene, using methylaluminoxane (MAO) and diethylaluminum chloride (DEAC) as catalyst activators.

2. Experimental

2.1. General methods

All manipulations were performed under an argon atmosphere by using standard Schlenk techniques. Toluene and THF were distilled from Na/benzophenone prior to use. Dichloromethane was distilled over calcium hydride. The water contents of these solvents were periodically controlled by Karl-Fischer coulometry by using a Methrom 756 KF apparatus. Argon and ethylene of special-purity grade were dried by purging through a column filled with 5 Å molecular sieves.

Ligand 2,6-bis(diphenylhydroxymethyl)pyridine was synthesized as described in [31]. Its physicochemical characteristics and ¹H and ¹³C NMR spectra match the published data. Phenylimidovanadium (V) chloride was prepared as described in [32]. VOCl₃, VCl₃*3THF, and CrCl₃*3THF as well as solutions of diethylaluminum chloride and butyllitium (Aldrich) were used. Polymethylaluminoxane (Witco) was used as a 10% solution in toluene.

NMR spectra were recorded on Bruker WP-600 and Bruker AMX-400 instruments. Deuterated solvents (CD_2Cl_2 , $CDCl_3$) were degassed by freeze-thaw-vacuum cycles and stored over 3 Å molecular sieves. Chemical shifts are reported in ppm vs. SiMe₄ and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz.

IR spectra were recorded on a Magna-IR 750 spectrophotometer. Elemental analysis was performed on Carlo Erba-1106 and Carlo Erba-1108 instruments.

The gel chromatograms of polymer samples were analyzed on a Waters GPCV-2000 chromatograph with the use of a PLgel 5 μ m MIXED-C column in 1,2,4-trichlorobenzene at 135 °C. Molecular masses were estimated using the universal calibration curve plotted relative to polystyrene standards.

The thermogravimetric analysis of samples was performed on a NETZSCHSTA-Jupiter449 C instrument. Measurements were carried out in a flow of argon (100 ml/min) in the temperature range 40–300 °C. The heating rate was 5 °C/min.

The experiments on the polymerization of ethylene were performed in a 100-ml reactor (Parr Instrument Co.).

X-ray diffraction data for the single crystals of 3, 4, 6, and 8 were collected using a "Bruker SMART APEX2" CCD diffractometer. The obtained images were integrated [33]. The precise unit cell dimensions and errors were determined. The absorption correction was applied semiempirically using the sadabs program [34]. The details of X-ray data collection in the subsequent refinement are listed in Table 2. Initially spherical atom refinements were undertaken with SHELXTL PLUS 5.0 [35] using the full-matrix least-squares method. All non-hydrogen atoms were allowed to have an anisotropic thermal motion. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center with numbers CCDC 878807-878810. X-ray diffraction analysis of polymers was performed on a DRON-2 instrument (Cu Ka radiation, Ni filter, a scan rate of 1 deg $(2\theta)/min$). The degree of crystallinity γ of samples was estimated from the ratio of the integral intensity of crystalline constituent and the total intensity.

2.2. Polymerization of ethylene

All operations on equipment preparation, the order and techniques of loading of gaseous ethylene and complexes, and the measurement of kinetic parameters of polymerization are similar to those described in [31].

The polymerization of ethylene was performed at a total pressure of ethylene and toluene vapors of 1.7 atm. Polymerization was carried out in a 100-ml reactor (PARR) equipped with a magnetic stirrer and inlets for loading components of catalytic systems and ethylene. Toluene (50 ml) and the necessary amount of a cocatalyst (DEAC or MAO) in the form of toluene solutions were successively loaded in the reactor together with the cocatalyst. The required amount of the precatalyst in the form of toluene solution was placed into a special syringe connected with the reactor. The reactor was heated to a specified temperature, and the reaction mixture was saturated with ethylene. Polymerization was started by precatalyst loading to the reaction mixture. The pressure of ethylene was maintained constant during polymerization. Polymerization was stopped through the addition of 10% HCl solution in ethanol to the reactor. The polymer was filtered off, washed several times with water-ethanol mixture, and dried under vacuum at 50-60 °C until a constant weight was achieved.

2.3. Synthesis

2.3.1. [2,6-(CPh₂OH)₂Py]CrCl₃ (3)

A two-necked flask equipped with a magnetic stirrer was successively charged in a flow of argon with ligand 1 (221.5 mg, 0.5 mmol), toluene (10 ml), and $CrCl_3$ *3THF (187 mg, 0.5 mmol). The reaction mixture was stirred at 40 °C for 100 h. The precipitated green crystals were filtered off and washed with methylene chloride and toluene.

Yield 0.09 g (32%); Anal. Calc. for $C_{31}H_{25}Cl_3NO_2Cr$: C, 61.80; H, 4.10; Cl, 17.69; N, 2.33; Cr, 8.64. Found: C, 61.75; H, 3.95; Cl, 17.73; N, 2.32; Cr, 8.66%. IR, v, cm⁻¹: (OH_{bound}) 3480, (Cr–O) 657 and (Cr–N) 583.

2.3.2. [2,6-(CPh₂O)₂Py]Cr[2-(CPh₂O)-6-(CPh₂OH)-Py] (**4**)

A two-necked flask equipped with a magnetic stirrer was successively charged in a flow of argon with ligand **1** (221.5 mg, 0.5 mmol) dissolved in toluene (5 ml) and $CrCl_3*3THF$ (93.5 mg, 0.25 mmol) dissolved in tetrahydrofuran (5 ml). The reaction mixture was stirred at 40 °C for 100 h. Precipitated blue crystals were filtered off and washed with tetrahydrofuran and toluene.

Yield, 0.21 g (45%); *Anal.* Calc. for $C_{62}H_{47}N_2O_4Cr$: C, 79.55; H, 5.06; Cr, 5.55; N, 2.99. Found: C, 79.27; H, 5.42; Cr, 5.29; N, 2.44%. IR, ν , cm⁻¹: (OH_{bound}) 3440, (O–Cr–O) 750, (Cr–O) 620, and (Cr–N) 560.

2.3.3. [2,6-(CPh₂O)₂Py]CrCl (5)

A two-necked flask equipped with a magnetic stirrer was charged in a flow of argon with compound **1** (221.5 mg, 0.5 mmol) and toluene (10 ml); then, at -78 °C, 2.5 M solution of butyllithium in *n*-hexane (0.44 ml, 1.1 mmol) was added dropwise. The reaction solution was slowly heated to room temperature, stirred for 4 h and cooled to -78 °C. CrCl₃, 3THF (187 mg, 0.5 mmol) dissolved in tetrahydrofuran (3 ml) was added, and the resulting mixture was stirred off, the organic solvents were evaporated, and the product formed was recrystallized from methylene chloride.

Yield, 0.11 g (80%); T_{melt} = 307 °C; Anal. Calc. for C₃₁H₂₃NO₂CrCl: C, 70.39; H, 4.38; Cl, 6.70; Cr, 9.83; N, 2.65. Found: C, 69.50; H, 5.03; Cl, 6.15; Cr, 9.40; N, 2.50%. IR, v, cm⁻¹: (Cr–O) 689 and (Cr– N) 547.

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Table 1

Crystallographic data and structure refinement details for **3**, **4**, **6** and **8**.

	3	4	6	8
Formula	C ₃₉ H ₄₁ Cl ₃ CrNO ₄	C ₁₃₅ H ₁₁₀ Cr ₂ N ₄ O ₉	C ₃₉ H ₄₀ Cl ₂ NO ₄ V	C ₃₁ H ₂₃ ClNO ₃ V
Μ	746.08	2036.27	708.56	204.06
T (K)	100(2)	100(2)	100(2)	100(2)
Space group	P2 ₁ /c	ΡĪ	ΡĪ	Сс
a (Å)	13.172(2)	12.7934(5)	15.050(2)	10.5834(10)
b (Å)	17.525(4)	12.8886(5)	21.834(3)	15.1756(10)
c (Å)	16.410(3)	16.6146(7)	22.090(3)	16.0379(12)
α (°)		103.038(2)	83.905(3)	
β(°)	111.640(5)	98.875(2)	70.256(3)	102.386(2)
γ (°)		96.789(2)	89.896(3)	
V (Å ³)	3521.4(11)	2603.45(18)	6789.0(16)	2515.9(3)
Ζ	4	2	8	4
ho (g cm ⁻³)	1.407	1.299	1.386	1.436
μ (Mo Ka), (mm $^{-1}$)	0.595	0.275	0.492	0.535
F(000)	1556	1068	2960	1120
Absorption correction (Mo Ka)	semiempirical from	semiempirical from	semiempirical from	semiempirical from
	equivalents	equivalents	equivalents	equivalents
Scan technique	ω -scan with 0.5 step	ω -scan with 0.5 step	ω -scan with 0.5 step	ω -scan with 0.5 step
θ_{\max}	27	29	29	29
Number of collected reflns	20254	31 409	79971	14763
Number of independent reflections (R_{int})	7667 (0.2029)	13822 (0.0423)	35931 (0.2249)	6610 (0.0389)
Number of observed reflections with	2605	8976	10222	4766
$[I>2\alpha(I)]$				
wR_2	0.1089	0.0962	0.2432	0.1546
R ₁	0.0542	0.0550	0.1050	0.0576
Goodness-of-fit (GOF) on F^2	0.703	1.091	0.872	1.000
$ ho_{ m max.}/ ho_{ m min}$ (e Å ⁻³)	0.430 and -0.582	0.356 and -0.735	0.898 and –1.154	0.596 and -0.748

Table 2

Catalytic activity of vanadium complexes with 2,6-bis(diphenylhydroxymethyl)pyridyl ligand activated by different cocatalysts (toluene solvent, an ethylene pressure of 1.7 atm, 30 °C, and a time of reaction of 30 min).

Run	Pre-catalyst	Cocatalyst, reactivator [V]/[Al]/[R-Cl]	Activity [kg of PE (mol of V) ^{-1} h ^{-1}]	$T_{\rm g}^{\rm a}$ (°C)	Crystallinity degree ^a (%)
1	6	Et ₂ AlCl (1/300)	0		
2	7	MAO (1/300)	trace		
3	7	Et ₂ AlCl (1/100)	trace		
4	7	Et ₂ AlCl (1/300)	139	148	60
5	7	Et ₂ AlCl (1/500)	153		
6	7	Et ₂ AlCl (1/1000)	187		
7	7	Et ₂ AlCl/MTCA (1/300/35)	544	150	54
8	7	Et2AlCl/MTCA (1/300/300)	579	139	60
9	8	MAO (1/300)	trace		
10	8	Et ₂ AlCl (1/100)	trace		
11	8	Et ₂ AlCl (1/300)	255	140	45
12	8	Et ₂ AlCl (1/500)	442		
13	8	Et ₂ AlCl (1/1000)	306		
14	8	Et ₂ AlCl/MTCA (1/300/300)	499		
15	9	$Et_2AlCl(1/300)$	102		
16	9	Et ₂ AlCl (1/500)	85	138	45
17	9	Et ₂ AlCl (1/1000)	85		
18	9	Et ₂ AlCl/MTCA (1/300/300)	360		

^a Melting temperatures and crystallinities determined by DSC at second heating of PE samples.

2.3.4. [2-(CPh₂O)-6-(CPh₂OH)-Py]VCl₂*THF (6)

A two-necked flask equipped with a magnetic stirrer was successively charged in a flow of argon with ligand **1** (221.5 mg, 0.5 mmol), toluene (10 ml), and VCl₃*3THF (187 mg, 0.5 mmol). The reaction mixture was stirred at 40 °C for 70 h. The green precipitate was filtered off and recrystallized from methylene chloride.

Yield 0.14 g (43%); *Anal.* Calc. for $C_{35}H_{32}NO_3VCl_2$: C, 66.05; H, 5.07; Cl, 11.14; N, 2.20; V, 8.00. Found: C, 66.02; H, 4.92; Cl, 11.07; N, 2.15; V, 7.91%. ¹H NMR (400 MHz, CDCl₃, 298 K): $\delta = 1.69$ [m, 4H, -CH₂ THF], 3.52 [m, 4H-CH₂ THF], 3.70 [s, 1H], 7.03-7.42 [m, 22H], 7.95 [t, *J* = 7.8 Hz, 1H]. IR, ν , cm⁻¹: (OH_{bound}) 3517, (V–O) 630, and (V–N) 575.

2.3.5. [2,6-(CPh₂O)₂ Py]VCl (7)

A two-necked flask equipped with a magnetic stirrer was charged in a flow of argon with ligand **1** (221.5 mg, 0.5 mmol)

and toluene (10 ml); then, at -78 °C, 2.5 M solution of butyllithium in *n*-hexane (0.44 ml, 1.1 mmol) was added dropwise. Then the reaction solution was slowly heated to room temperature, the resulting mixture was stirred for 4 h and cooled to -78 °C, and VCl₃*3THF (187 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 20 h. Inorganic products were filtered off, and the organic solvents were evaporated. The green complex formed was recrystallized from toluene.

Yield, 0.14 g (52%); *Anal.* Calc. for $C_{31}H_{23}NO_2VCI$: C, 70.53; H, 4.39; Cl, 6.72; N, 2.65; V, 9.65. Found: C, 69.02; H, 4.27; Cl, 6.29; N, 2.49; V, 9.50%. ¹H, (CDCl₃) 7.25–7.94 (m, 23HAr). IR, ν , cm⁻¹: (V–O) 657 and (V–N) 583.

2.3.6. [2,6-(CPh₂O)₂Py]V(O)Cl (8)

A two-necked flask equipped with a magnetic stirrer was charged in a flow of argon with ligand **1** (221.5 mg, 0.5 mmol) and toluene (10 ml); then at -78 °C a solution of butyllithium

(2.5 M in *n*-hexane, 0.44 ml, 1.1 mmol) was added dropwise. Then the reaction solution was slowly heated to room temperature, the mixture was stirred for 4 h and cooled to -78 °C, and VOCl₃ (0.05 ml, 0.5 mmol) was added. The resulting mixture was stirred at room temperature for 12 h, inorganic products were filtered off, and the organic solvents were evaporated. The yellow complex formed was recrystallized from methylene chloride.

Yield, 0.10 g (32%); *Anal.* Calc. for $C_{31}H_{23}CINO_3V$: C, 68.45; H, 4.26; Cl, 6.52; N, 2.85; V, 9.37. Found: C, 68.67; H, 4.27; Cl, 6.51; N, 2.86; V, 9.34%. ¹H, (CDCl₃) 7.19–7.70 (m, 22H), 8.05 (t, *J* = 7.7 Hz, 1H–Ar).IR, *v*, cm⁻¹: (V–O) 630, (V–N) 521, and (V–Cl) 450.

2.3.7. [2,6-(CPh₂OH)₂Py]V(NPh)Cl (9)

A two-necked flask equipped with a magnetic stirrer was charged in a flow of argon with ligand **1** (221.5 mg, 0.5 mmol) and toluene (5 ml); then, at -78 °C a solution of butyllithium (2.5 M in *n*-hexane, 0.44 ml, 1.1 mmol) was added dropwise. Then the reaction solution was slowly heated to room temperature, the mixture was stirred for 4 h and cooled to -78 °C, and VCl₃NPh (124 mg, 0.5 mmol) dissolved in toluene (5 ml) was added. The resulting mixture was stirred at room temperature for 20 h, inorganic products were filtered off, and the organic solvents were evaporated. The green product formed was recrystallized from toluene.

Yield, 0.13 g (42%); Anal. Calc. for $C_{37}H_{28}ClN_2O_4V$: C, 71.79; H, 4.56; Cl, 5.73; N, 4.53; V, 8.23. Found: C, 71.60; H, 4.55; Cl, 5.74; N, 4.52; V, 8.24%. IR, ν , cm⁻¹: (V–O) 630, and (V–N) 548.

3. Results and discussion

3.1. Synthesis and structure of chromium and vanadium complexes

Direct interaction of ligand **1** with tetrahydrofuran complex of chromium (III) chloride leads to either chelate **3** or to the coordination-saturated octahedral complex **4** (Fig. 1), depending on the amount of metal halide.

The structure of chelate **3**, in which protons of the hydroxyl groups are retained, is shown in Fig. 2.



Fig. 1. General synthesis of chromium (III) complex compounds with 2,6-bis(diphenylhydroxymethyl)pyridyl ligand.

Distorted tetragonal bipyramidal environment of the chromium atom consists of three chlorine atoms and pyridyl nitrogen atom in its equatorial plane and two oxygen atoms in axial position (see Fig. 2). CrCl₃N fragment is almost plane; the maximum shift of atoms from the plane does not exceed 0.01 Å. The polyhedron distortion can be characterized by O(1)-Cr(1)-O(2) angle of 155.58(14)°, which significantly deviates from 180°. Chromiumchlorine bonds are similar to each other: their lengths vary between 2.3022(17) and 2.3225(18) Å, which is a mean value for Cr-Cl bonds for this class of compounds. The Cr-N bond between the metal atom and pyridine ligand (2.004(4)Å) is among the shortest of its kind according to Cambridge Structural Database data. The shortening of this bond is due to polydentate chelating character of the ligand. Cr-N distance in the complexes of "free" pyridine is about 2.10–2.15 Å [35]. Both Cr–O bonds have a length of 2.013(4) Å which is in good agreement with the equal degree of oxygen atoms protonation. Moreover, both OH groups are involved into similar H-bonds with outer-sphere tetrahydrofuran solvent molecules (0...0 distances are 2.640(5) and 2.555(5) Å, and OHO angles are 155° and 174° for $O(1)-H(10)\cdots O(2S)$ and O(2)- $H(20) \cdots O(1S)$, respectively).

The IR spectrum of complex **3** exhibits bands at 3404 cm⁻¹ due to the stretching vibrations of coordinated hydroxyl groups. The resulting bands for stretching vibrations of Cr–O and Cr–N groups manifest themselves at 640 and 594 cm⁻¹, respectively.

The DSC-TGA study of the thermal properties of compound **3** revealed weight losses at 137 and 175 °C which, in principle, correspond to the stepwise elimination of two HCl molecules.

The interaction of two equivalents of the ligand with one equivalent of CrCl₃, 3THF yielded coordination-unsaturated complex **4**, which structure was studied by X-ray diffraction analysis (Fig. 3).

In this complex the tetragonal bipyramidal environment of the chromium atom is significantly distorted: the shift of chromium atom from the equatorial plane O(1)O(2)N(1)N(2) is about 0.1 Å. O(3)-Cr(1)-O(4) axial angle is 156.54(6)°. Geometrically, two types of Cr–O bonds can be detected in complex 4: Cr(1)-O(1) and Cr(1)-O(4) bond are 0.1 Å shorter (1.9099(13) Å and 1.9167(14)°) than Cr(1)-O(2) and Cr(1)-O(3) bonds (2.0310(13) and 2.0205(14)Å. respectively). The above value of 2.013(4) Å in 3 is somewhat between two types of Cr–O bonds in **4**. At this moment we cannot unambiguously explain this phenomenon. One possibility is the difference in bond length can be attributed to the general weakness of coordinate bonds in the complexes with high coordination numbers. It was previously postulated that the variation of metalligand bond lengths in such complexes may be chaotic and to some extent unpredictable [36]. In contrast, the Cr-N bond lengths in the complex are virtually identical with the lengths of 1.9930(15) and 1.9976(15) Å for Cr(1)–N(2) and Cr(1)–N(1), respectively.

Unlike the spectrum of the free ligand, the IR spectrum of the complex **4** exhibits bands at 750 and 620 cm⁻¹ due to the stretching vibrations of O–Cr–O and of Cr–O, respectively; the bands corresponding to Cr–N bonds are observed at 560 cm⁻¹. The band corresponding to the stretching vibrations of the bound hydroxyl group appears at 3340 cm⁻¹. The obtained complex is thermally stable, and its decomposition begins only at 130 °C.

The use of the ligand preliminary deprotonated by butyl lithium in complex formation yielded compound **5**. The structure of this compound was studied by elemental analysis and IR spectroscopy.

As in the case of chromium chloride, the direct interaction of ligand **1** with VCl₃, 3THF yields proton-containing complex **6** (Fig. 5). The structure of this complex is shown in Fig. 3a. The reaction of dilithium salt of ligand **2** with vanadyl chloride yields complex **8**. Its structure is presented in Fig. 5.

Coordination polyhedron of vanadium atom in compound **6** is that of a distorted tetragonal bipyramid. In this complex two chloride ligands in equatorial plane show considerably weaker bonding

Please cite this article in press as: D.A. Kurmaev et al., Inorg. Chim. Acta (2013), http://dx.doi.org/10.1016/j.ica.2012.11.006

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Fig. 2. The structure of complex 3 according to single-crystal X-ray diffraction study.



Fig. 3. The structure of complex 4 according to single-crystal X-ray diffraction study.

than in **8** (2.294(2) and 2.322(2) Å for Cl(1) and Cl(2) in **6** versus 2.1858(14) Å in **8**), which is in agreement with different types of coordination polyhedra, as well as a higher coordination number of vanadium in **6**. V–N bonds in both complexes are ca. 2.05 Å. Equatorial V–O(THF) bond is considerably weaker than two axial ones (2.150(4) Å versus 1.812(4) and 1.798(4) Å), which is in agreement with additional coordination character of THF.

According to the IR data, the stretching vibrations of the coordinated hydroxyl group in complex **6** show a low-frequency shift relative to the unbound group and are observed at 3364 cm^{-1} .

The reaction of vanadium (III) tetrahydrofuran complex with dilithium salt of the ligand produces compound **7**. No hydroxyl groups absorption bands are observed in the IR spectrum of this complex. Compound **7** is very sensitive to oxygen. During storage even in the crystalline state, it gradually transforms into compound **8**. That is evident from the crystals color change from green to yellow, which is typical for V (V) compounds.

Therefore, compound **7** is difficult to experiment with. As such, we could not perform high-quality structural experiments, and all experiments on the catalytic activity of **7** were carried out *in situ*; that is, complex **7** was not isolated from the reaction mixture.

As known from the literature [37,38], the replacement of V=O group by V=NPh group leads to an increase in stability and activity of vanadium-containing catalytic systems. In order to check the effect of such modification, compound **9** was prepared by the interaction of dilithium salt of 2,6-bis(diphenylhydroxymethyl)pyridine **2** with phenylimido vanadium (V) chloride (Fig. 4). Composition of compound **9** was evaluated only by elemental analysis and IR spectroscopy.

3.2. Polymerization of ethylene

Catalytic activity of obtained complexes was investigated in the model reaction of ethylene polymerization (toluene was used as a solvent, monomer pressure of 1.7 atm, temperature of 30 °C, and time of polymerization of 30 min). Precatalysts were activated using toluene solutions of MAO and DEAC.

The experiments showed that all the chromium complexes were not effective in ethylene polymerization experiments, performed with either type of activator ([Cr]/[Al] = 1: 300). The only exception was in the case of compound **5**, where trace amounts of polymer were observed. An increase of the reaction temperature to 70 °C, use of methylene chloride as a solvent, or the preactivation of catalyst for 1 h with a small excess of the organoaluminum cocatalyst did not increase its catalytic activity.

Data on vanadium precatalysts are listed in Table 2. Complex **6**, wherein the metal is linked to the ligand via coordination bonds solely, does not polymerize ethylene when DEAC used as an activator. Precatalysts **7–9** exhibit only minor activity, when activated by MAO ($AI_{MAO}/V = 300 \text{ mol/mol}$). DEAC, which is a conventional cocatalyst for Ziegler homogeneous vanadium systems, exhibits

considerably higher activating ability than MAO. The value of catalytic activity of all the precatalysts depends on the Al_{DEAC}/V molar ratio.

Precatalyst **7** tends to gradually increase its catalytic activity to the maximum value of 187 kg/(mol V h) at $Al_{DEAC}/V = 1000$ mol/ mol ratio. Precatalyst **8** demonstrates its maximum catalytic activity of 442 kg/(mol V h) at $Al_{DEAC}/V = 500$ mol/mol ratio. A further increase in Al_{DEAC}/V to 1000 mol/mol results in a drop of the activity by a factor of 1.4. The maximum catalytic activity of precatalyst **9** is rather low (102 kg/(mol V h) at $Al_{DEAC}/V = 300$), and tends to decrease to 85 kg/(mol V h) at $Al_{DEAC}/V = 500$ and 1000 mol/mol ratios. All precatalysts show the trace activity at $Al_{DEAC}/V = 100$. Considerable differences in activities of precatalysts **7–9** are possibly due to the differences in their reduction abilities resulting in species inactive in polymerization reactions. At the same time, it should be noted that the presence of hydroxypyridyl ligands in complexes **7–9** makes vanadium atoms more resistant to



Fig. 4. Synthesis of complex compounds of vanadium (III) and (V) with 2,6-bis(diphenylhydroxymethyl)pyridyl ligand.



Fig. 5. The structure of complexes 6 (a) и 8 (b) according to single-crystal X-ray diffraction study.

Please cite this article in press as: D.A. Kurmaev et al., Inorg. Chim. Acta (2013), http://dx.doi.org/10.1016/j.ica.2012.11.006

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Fig. 6. Thermograms of PE sample obtained with 7/DEAC/MTCA system (experiment 7) at first (solid line) and second (dashed line) heating.

reduction. Thus, in the case of ethylene polymerization with homogeneous VOCl₃/AlEt₂Cl catalytic system the catalyst is deactivated within a few minutes even at low molar ratio $Al_{DEAC}/V = 20$ due to reduction to V (II) species [24]. In our case complexes **7** and **8** are working much longer.

It was empirically demonstrated that activity of vanadium based Ziegler systems can be recovered by addition of small amounts of perchlorinated organics, specifically perchloropentadiene [39], and esters of trichloroacetic acid [40]. Most likely, these compounds act as oxidative reagents in the system which convert inactive species of V (II) to active ones containing V (III), V (IV), and V (V).

In order to verify the efficiency of post-metallocene systems reactivation, methyl trichloroacetate (MTCA) was added to the reaction solution. Approximately fourfold increase in the activity was observed for catalytic system **7**/DEAC, when 35 or 300 equivalents of MTCA relative to vanadium were added (cf. experiments 4 and 7, 8, Table 1). For complexes **8** and **9** the catalytic activity increased by factors of 2 and 4, at a molar ratio of MTCA/V = 300 (experiments 14, 11 and 18, 15), respectively. It is noteworthy that in the presence of MTCA the differences in catalytic activities of complexes **7**, **8**, and **9** are significantly smaller (578, 499 and 360) kg PE/(mol [V] h) than in the absence of reactivator (139, 255 and 102) kg PE/(mol [V] h). However, the introduction of phenylimido group introduces a significant loss in catalysts activity both in the presence of the activator and in its absence.

Ultra-high-molecular-weight PEs insoluble in 1,2,4-trichlorobenzene at 135 °C were obtained with all the vanadium catalysts. All PE samples are linear in structure. The absence of branches is evident from the absence of 1378 cm⁻¹ absorption band in FTIR spectra of polymer films. The band refers to symmetric bending of methyl groups in branches. As a result, these linear ultra-highmolecular-weight PE samples demonstrate very high melting temperatures and crystallinity. Thus PEs prepared with the system 7/DEAC both in the absence (experiment 4) and in the presence of 35 equivalents of TMCA (experiment 7) show very high melting temperatures (150-152 °C) and crystallinity which are not considerably changed at both first and second heating as demonstrated for PE obtained in experiment 7 (Fig. 6). An increase in the content of MTCA to 300 equivalents leads to some decrease in the PE melting temperature to 139 °C, with crystallinity standing high (experiment 7).



Fig. 7. Thermograms of PE samples obtained with (1) 7/DEAC, (2) 8/DEAC, and (3) 9/DEAC catalytic systems (experiments 4, 11, and 16 in Table 1).

The morphology of nascent polymers depends on the nature of precatalysts. Thus, the DSC curves of PEs prepared with precatalysts **7** and **8** demonstrate single melting peaks at 148 and 140 °C (Fig. 7, curves 1, 2), respectively; while the DSC curve of PE obtained with precatalyst 9 reveals two pronounced peaks at 145 and 135 °C (curve 2). After recrystallization during the second heating, the thermogram of the polymer exhibits only one peak at 138 °C (experiment 16).

4. Conclusion

New chromium (III), vanadium (III) and (V) complexes were synthesized and characterized. Depending on the nature of the metal and the synthesis conditions, there are various types of coordination state of the terdentate pyridine ligand **1** in the obtained complexes: it can bind either as a dianionic, bisalkoxide, terdentate (compounds **5**, **7**, **8**, **9**), monoanionic, alkoxide/alkohol, terdentate (compounds **4**, **6**) or as a neutral, bisalkohol, terdentate ligand (compound **3**).

Please cite this article in press as: D.A. Kurmaev et al., Inorg. Chim. Acta (2013), http://dx.doi.org/10.1016/j.ica.2012.11.006

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The activation of these complexes with DEAC as cocatalyst was performed to evaluate their performances as ethylene polymerisation catalysts. All chromium complexes were inactive. Vanadium (III) and (V) complexes act as rather stable and efficient catalysts for ethylene polymerization. It was demonstrated that small excesses of a reactivator – methyl trichloroacetate, can significantly increase the activity of catalytic systems. With all other factors being the same, the vanadium (V) complexes have the superior activity when compared to vanadium (III) complexes. However, application of a reactivator levels off this difference.

Acknowledgments

We are grateful to Russian Foundation for Basic Research (project nos. 11-03-12172, 11-03-00297 and 12-03-00974, Ph.D. A.V Dunaev for thermogravimetric analysis of coordination compounds and polymers and Ph.D. A.A. Korlyukov for X-ray diffraction analysis of polymers.

Appendix A. Supplementary material

CCDC 878807–878810 contains the supplementary crystallographic data for **3**, **4**, **6** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2012.11.006.

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