

# Preparation, structure and ethylene polymerization behavior of mixed-halide nickel(II) complexes and cobalt(II) complex containing imidazolium

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Received 4 January 2005; revised 26 February 2005; accepted 11 March 2005

Available online 19 April 2005

Dedicated to Professor Quan-Xin Xin on the occasion of his 70th birthday

## Abstract

Preparation of two imidazolium salts, two monomeric nickel(II) and one cobalt(II) complexes bearing imidazolium ligands is described. The solid-state structures of these compounds have determined by single-crystal X-ray diffraction. After activation with methylaluminoxane (MAO) the nickel complexes show moderate catalytic activities of up to  $6 \times 10^5$  g PE mol<sup>-1</sup>Ni h<sup>-1</sup> for polymerization of ethylene. Catalytic activities, molecular weights have been investigated under the various reaction conditions.

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*Keywords:* Imidazolium salts; Nickel; Cobalt; Homogeneous catalysts; Polymerization; Polyethylene

## 1. Introduction

The recent emergence of highly active late-transition-metal-based catalysts for polymerizing ethylene has introduced a new dimension in the search for novel olefin polymerization catalysts. These catalysts operate under less stringent reaction conditions and can tolerate polar functional group in the monomer; hence they have the potential to widen the scope of polyolefins assessable by metal-based catalytic technology [1–5]. Nickel catalysts have provided some of the most significant advances in late transition metal olefin polymerization catalysis and have given some of the most promising results [6–8]. Recently we have reported several novel nickel-based olefin polymerization catalysts [9,10]. In or-

der to extend the range of polyolefinic materials produced considerable effort have been devoted to the discovery of new families of catalysts.

Due to their unique physical and chemical properties imidazolium cations and their counteranions have currently received much attention as ionic liquid which have suggested for a wide range of applications including in the fields of organic syntheses and biphasic catalysis [11] and in other areas, e.g., surfactants [12], electrochemistry [13], separations [14], and photochemistry [15]. Metal-containing imidazolium salts are rather rare [16,17] and most often contain rather complex anions where the metal resides [18–21]. So we take interest into the synthesis and catalytic properties of this kind of metal-containing imidazolium complexes.

The present paper reports the results of our studies on the polymerization of ethylene catalyzed by a new family of metal-containing imidazolium catalyst precursors.

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## 2. Experimental

### 2.1. General procedures

All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Methanol was dried over Mg, CH<sub>2</sub>Cl<sub>2</sub> over CaH<sub>2</sub>, and then distilled under nitrogen immediately prior to use. Methylaluminoxane (MAO), 1-methylimidazole and 2-picolychloride hydrochloride were purchased from Witco and Acros, respectively. Other solvents were used as received as technical grade solvents. 1-Benzylimidazol were prepared according to the literatures [22]. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a VAVCE-DMX 500 Spectrometer in CDCl<sub>3</sub>, MeOH-d, DMSO-d. <sup>13</sup>C NMR spectra of polyethylene were obtained using *o*-dichlorobenzene as a solvent on FX-100 NMR spectrometer at 130 °C. Elemental analysis was performed on Elementar III vario EI Analyzer.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 3-methyl-1-picolyimidazolium iodide (1)

To a solution of picolyl chloride (5.85 mmol, prepared by basifying 0.96 g of picolyl chloride hydrochloride) in 20 mL of acetone were added 1-methylimidazole (0.470 mL, 5.89 mmol) and NaI (0.88 g, 5.9 mmol). After it was stirred for 48 h, the solution was filtered through Celite and the solvent was removed in vacuum to afford a thick brown syrup. The syrup was re-dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> and the solution was filtered to remove residual NaCl. Addition of 25 mL ether caused an oil to separate out. The solvent was decanted off, and then the resulted oil was taken up in 8 mL of CH<sub>2</sub>Cl<sub>2</sub>, and 20 mL of ether was added to precipitate the product. The oily solid that formed was triturated for 2 h and the resultant powder washed with 10 mL of ether. Yield: 1.22 g (69%). <sup>1</sup>H NMR (500 MHz, DMSO-d, ppm): δ 10.31 (s, 1H, NC(H)N), 8.56 (s, 1H, pyridyl), 7.83 (m, 2H, pyridyl), 7.62 (s, 1H, HCCH), 7.32 (s, 1H, HCCH), 7.26 (m, 1H, pyridyl), 5.74 (s, 1H, NCH<sub>2</sub>), 4.07 (s, 3H, NCH<sub>3</sub>).

#### 2.2.2. Synthesis of 3-benzyl-1-picolyimidazolium iodide (2)

Analogous to the synthesis of **1** but using picolyl chloride (5.85 mmol), 1-benzylimidazole (0.925 g, 5.85 mmol) and NaI (0.88 g, 5.9 mmol) in 20 mL of acetone, give **2** as a red solid. Yield: 1.32 g (60%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 10.32 (s, 1H, NC(H)N), 8.56 (m, 1H, pyridyl), 7.80 (d, 2H, HCCH), 7.66 (d, 1H, pyridyl), 7.43 (m, 7H, pyridyl, Ph), 5.74 (s, 2H, CH<sub>2</sub>Ph), 5.57 (s, 2H, NCH<sub>2</sub>).

#### 2.2.3. Ni[3-methyl-1-picolyimidazolium]Cl<sub>2.5</sub>I<sub>0.5</sub> (3)

A stirred DMSO solution (5.0 mL) of 3-methyl-1-picolyimidazolium iodide (301 mg, 1 mmol) and anhydrous NiCl<sub>2</sub> (130 mg, 1 mmol) was heated to 140 °C for 2 days, during which time the reaction solution had bleached to green. The remaining DMSO was then removed in vacuo at 50 °C to give a green solid, which was re-crystallized with MeOH/Et<sub>2</sub>O to give green crystals. Yield: 0.292 g (76%). <sup>1</sup>H NMR (500 Hz, DMSO-d, ppm): δ 9.33 (s, 1H, NC(H)N), 8.64 (s, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.91 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.80 (s, 1H, HCCH), 7.75 (s, 1H, HCCH), 7.55 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.40 (s, 1H, C<sub>5</sub>H<sub>4</sub>N), 5.58 (s, 2H, NCH<sub>2</sub>), 3.90 (s, 3H, NCH<sub>3</sub>). Anal. Calc. for C<sub>10</sub>H<sub>12</sub>Cl<sub>2.5</sub>I<sub>0.5</sub>N<sub>3</sub>Ni: C, 31.18; H, 3.12; N, 10.91. Found: C, 31.43; H, 3.50; N, 10.42%.

#### 2.2.4. Ni[3-benzyl-1-picolyimidazolium]Cl<sub>2.5</sub>I<sub>0.5</sub> (4)

This complex was prepared in a manner analogous to that described above, using **2** (377 mg, 1 mmol) and NiCl<sub>2</sub> (130 mg, 1 mmol) in 5 mL of DMSO, and then re-crystallized with MeOH/Et<sub>2</sub>O to yield green crystals. Yield: 0.368 g (80%). <sup>1</sup>H NMR (500 Hz, DMSO-d, ppm): δ 9.52 (s, 1H, NC(H)N), 8.60 (s, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.91 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.86 (m, 1H, HCCH), 7.83 (s, 1H, HCCH), 7.54 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.44 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.43 (m, 5H, Ph), 5.60 (s, 2H, CH<sub>2</sub>Ph), 5.50 (s, 2H, NCH<sub>2</sub>). Anal. Calc. for C<sub>16</sub>H<sub>16</sub>Cl<sub>2.5</sub>I<sub>0.5</sub>N<sub>3</sub>Ni: C, 41.66; H, 3.47; N, 9.11. Found: C, 42.42; H, 3.59; N, 8.86%.

#### 2.2.5. Co[3-methyl-1-picolyimidazolium]Cl<sub>3</sub> (5)

This complex was prepared in a manner analogous to that described above, using **1** (300 mg, 1 mmol) and CoCl<sub>2</sub> (130 mg, 1 mmol) in 5 mL of DMSO, and then recrystallized with MeOH/Et<sub>2</sub>O to yield blue crystals. Yield: 0.244 g (72%). <sup>1</sup>H NMR (500 Hz, MeOH-d, ppm): δ 9.20 (s, 1H, NC(H)N), 8.54 (d, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.88 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.65 (d, 1H, HCCH), 7.50 (d, 1H, HCCH), 7.43 (m, 2H, C<sub>5</sub>H<sub>4</sub>N), 5.56 (s, 2H, NCH<sub>2</sub>), 3.45 (s, 3H, NCH<sub>3</sub>). <sup>13</sup>C NMR (500 MHz, MeOH-d): δ 152.9 (pyridyl, C2), 148.9 (pyridyl, C6), 137.3 (pyridyl, C4), 128.5 (NCN), 124.6 (pyridyl, C3), 124.0 (pyridyl, C5), 123.4 (NCCN), 122.7 (NCCN), 54.2 (NCH<sub>2</sub>), 35.3 (NCH<sub>3</sub>). Anal. Calc. for C<sub>10</sub>H<sub>12</sub>Cl<sub>3</sub>N<sub>3</sub>Co: C, 35.35; H, 3.53; N, 12.37. Found: C, 35.78; H, 3.22; N, 12.65%.

### 2.3. X-ray crystallography

Suitable crystals for X-ray analysis of **2**, **4** and **5** were obtained by slow diffusion of diethyl ether into methanol solutions of the corresponding compound, respectively. X-ray intensity data were collected on the CCD-Bruker SMART APEX system. The determination of the unit cell and the collection of intensity data were performed with graphite-monochromated Mo K $\alpha$

radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All the data were collected at room temperature using the  $\omega$  scan technique. The structures were solved by direct methods, using Fourier techniques, and refined on  $F^2$  by a full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included but not refined. All the calculations were carried out using the program SHELXTL. Crystal data, data collection parameters, and the results of the analyses of compounds **2**, **4** and **5** are listed in Table 1.

#### 2.4. Ethylene polymerization

Ethylene polymerization with the nickel catalysts at 1 atm of ethylene pressure was performed in a 200-mL Schlenk-type glass reactor fitted with a mechanical stirrer. After being flame-dried three times, the flask was back-filled with ethylene. Then the reactor was charged with 45 mL of toluene and desired MAO (10%) via syringe under an atmosphere of nitrogen. After the catalyst in 5 mL of solvent was introduced into the polymerization bottle via syringe, stirring was begun and the polymerization was kept at a desired temperature. The reaction flask was immersed in a certain temperature

water bath for 15 min prior to injection of the catalyst. After 30 min, the polymerization was quenched with ethanol/HCl and the polymer was isolated by filtration, dried in vacuum at 40 °C for 10 h.

The high-pressure polymerization with nickel catalysts was carried out in a 500-mL autoclave charged with 100 mL toluene under an atmosphere of argon. The catalyst was weighted out and added to the polymerization system. After three times of ethylene gas exchange, the ethylene pressure was raised to the specified value and maintained for a certain time. After 30 min, the polymerization was terminated by the addition of methanol and dilute HCl (10%). The solid polyethylene was filtered, washed with methanol and dried at 40 °C for 10 h in vacuum.

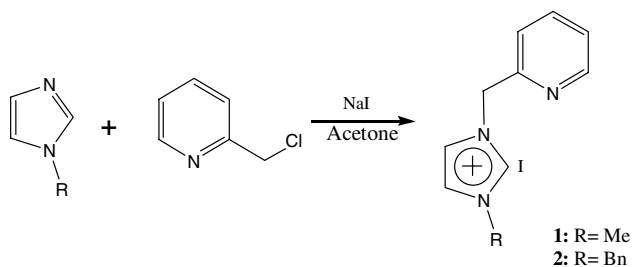
### 3. Results and discussion

#### 3.1. Synthesis and characterization

The functionalized imidazolium salts were synthesized by reacting picolyl chloride with the corresponding substituted imidazole according to Scheme 1.  $^1\text{H NMR}$

Table 1  
Summary of crystallographic data for **2**, **4** and **5**

	<b>2</b>	<b>4</b>	<b>5</b>
Chemical formula	$\text{C}_{16}\text{H}_{16}\text{IN}_3$	$\text{C}_{16}\text{H}_{16}\text{Cl}_{2.5}\text{I}_{0.5}\text{N}_3\text{Ni}$	$\text{C}_{20}\text{H}_{24}\text{Cl}_6\text{Co}_2\text{N}_6$
Formula weight	377.22	461.10	679.01
Temperature (K)	298(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2(1)2(1)2(1)$	$P\bar{1}$
Unit cell dimensions			
$a$ (Å)	8.920(3)	8.2617(10)	8.462(3)
$b$ (Å)	9.506(3)	13.6612(16)	11.958(4)
$c$ (Å)	9.630(3)	15.9364(19)	13.905(4)
$\alpha$ (°)	76.053(4)	90	99.616(4)
$\beta$ (°)	84.896(4)	90	98.718(4)
$\gamma$ (°)	77.858(4)	90	90.633(4)
Volume (Å <sup>3</sup> )	774.1(4)	1798.7(4)	1372.3(7)
$Z$	2	4	2
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.618	1.703	1.643
Absorption coefficient (mm <sup>-1</sup> )	2.062	2.309	1.815
$F(0\ 0\ 0)$	372	920	684
Crystal size (mm)	$0.55 \times 0.45 \times 0.40$	$0.20 \times 0.20 \times 0.15$	$0.15 \times 0.10 \times 0.10$
$\theta$ Range for data collection (°)	2.18–25.01	1.96–26.00	1.50–25.01
Limiting indices	$-10 \leq h \leq 9,$ $-11 \leq k \leq 7,$ $-11 \leq l \leq 11$	$-10 \leq h \leq 10,$ $-16 \leq k \leq 16,$ $-13 \leq l \leq 19$	$-10 \leq h \leq 9,$ $-14 \leq k \leq 11,$ $-11 \leq l \leq 16$
Reflections collected	3218	8279	5784
Independent reflections [ $R_{\text{int}}$ ]	2676 [0.0208]	3490 [0.0557]	4765 [0.0183]
Completeness to theta (°)	25.01 (98.1%)	26.00 (99.5%)	25.01 (98.6%)
Maximum and minimum transmission	0.4926 and 0.3967	0.7233 and 0.6553	0.8394 and 0.7725
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2676/0/246	3490/0/210	4765/0/309
Goodness-of-fit on $F^2$	1.064	0.847	1.039
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0343, wR_2 = 0.0919$	$R_1 = 0.0472, wR_2 = 0.1091$	$R_1 = 0.0385, wR_2 = 0.0912$
Largest difference peak and hole (e/Å <sup>3</sup> )	0.883 and $-1.040$	0.464 and $-0.617$	0.492 and $-0.296$

Scheme 1. Synthesis of **1** and **2**.

spectra of the ligands are in agreement with their assigned structures.

The neutral 3-*R*-1-picolylimidazolium transition-metal trihalide complexes **3**, **4** and **5** were prepared via an adaptation of straightforward procedure which utilized DMSO and long reaction time to give high yields of complexes (Scheme 2). Initial attempts to prepare complexes **3**, **4** and **5** by utilizing procedure according to the literature [23], involving reaction in THF resulted in mixtures of complexes **3**, **4** and **5** in yields less than ca. 10%, due to the poor solubility of  $MCl_2$  ( $M = Ni, Co$ ) in THF.

In the  $^1H$  NMR spectra of complexes **3**, **4** and **5**, significant up-field shift of about 1 ppm is observed for the NC(H)N proton when compared to those in the corresponding precursors. Chemical shifts of other protons are similar to those in the  $^1H$  NMR spectra of the corresponding precursors. Elemental analyses of the complexes are in agreement with their assigned structures.

The complexes **3**, **4** and **5** are soluble in DMSO and MeOH, sparingly soluble in  $CH_2Cl_2$ , insoluble in diethyl ether and hydrocarbon solvents. The complexes are moderately stable in dry air.

### 3.2. X-ray structure

The crystallographic data for complexes **2**, **4** and **5** are given in Tables 1 and 2. The ORTEP drawing of the compound **2** is shown in Fig. 1. The bond distances and angles of the compound are normal and are comparable with those reported for imidazolium and pyridines [24].

The ORTEP drawing of the compound **4** (Fig. 2) shows that the compound to be monomeric with the pic-

Table 2  
Selected bond lengths (Å) and angles (°) for **2**, **4** and **5**

Compound <b>2</b>			
N(1)–C(5)	1.317(4)	N(1)–C(1)	1.330(5)
N(2)–C(9)	1.330(4)	N(3)–C(9)	1.318(4)
C(5)–N(1)–C(1)	117.4(3)	N(3)–C(9)–N(2)	107.9(3)
Compound <b>4</b>			
Ni(1)–N(1)	2.031(6)	Ni(1)–Cl(3)	2.255(2)
Ni(1)–Cl(2)	2.2976(17)	Ni(1)–Cl(1)	2.321(2)
N(1)–Ni(1)–Cl(3)	107.58(17)	N(1)–Ni(1)–Cl(2)	103.90(17)
Cl(3)–Ni(1)–Cl(2)	114.13(8)	N(1)–Ni(1)–Cl(1)	106.10(18)
Cl(3)–Ni(1)–Cl(1)	110.07(8)	Cl(2)–Ni(1)–Cl(1)	114.33(7)
Compound <b>5</b>			
Co(1)–N(1)	2.084(3)	Co(1)–Cl(3)	2.2421(13)
Co(1)–Cl(1)	2.2505(12)	Co(1)–Cl(2)	2.2653(13)
Co(2)–N(4)	2.087(3)	Co(2)–Cl(5)	2.2381(13)
Co(2)–Cl(6)	2.2400(12)	Co(2)–Cl(4)	2.2563(11)
N(1)–Co(1)–Cl(3)	105.90(9)	N(1)–Co(1)–Cl(1)	106.33(9)
Cl(3)–Co(1)–Cl(1)	112.33(5)	N(1)–Co(1)–Cl(2)	111.27(9)
Cl(3)–Co(1)–Cl(2)	114.38(5)	Cl(1)–Co(1)–Cl(2)	106.41(5)
N(4)–Co(2)–Cl(5)	100.63(9)	N(4)–Co(2)–Cl(6)	107.13(9)
Cl(5)–Co(2)–Cl(6)	116.98(5)	N(4)–Co(2)–Cl(4)	115.59(9)
Cl(5)–Co(2)–Cl(4)	109.29(4)	Cl(6)–Co(2)–Cl(4)	107.44(4)

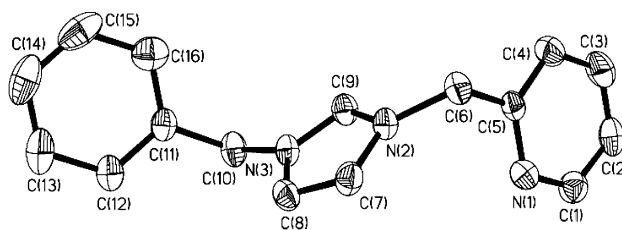
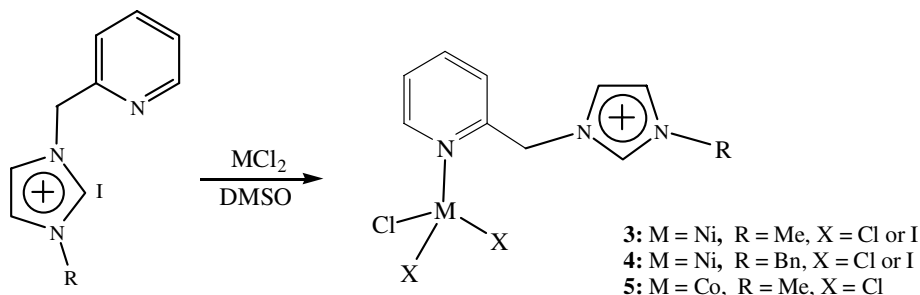


Fig. 1. Molecular structure of **2** (cation only) (The hydrogen atoms are omitted for clarity.)

olyl-functionalized imidazolium ligand bonding to the nickel(II) center through the nitrogen of pyridine. The remaining three coordination sites of the tetrahedral coordinated nickel center are occupied by halide anions. After location of reasonable positions for all halide atoms of the complex, refinement of the unique two apical sites as single sites fully occupied by either Cl or I resulted in unreasonably large or small, and also significantly elongated, displacement parameters. These

Scheme 2. Synthesis of **3**, **4** and **5**.

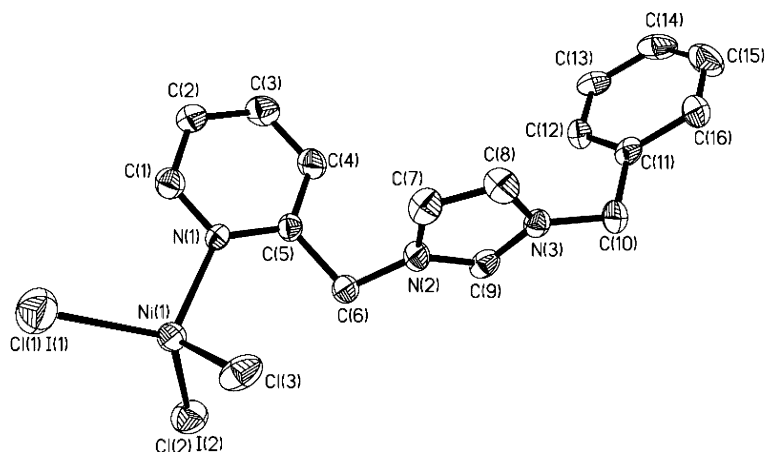


Fig. 2. Molecular structure of **4** (The hydrogen atoms are omitted for clarity.)

two sites were successfully modeled as split, mixed Cl/I positions. The affected halide sites are Cl1/I1 and Cl2/I2. The final refined occupancies are Cl1/I1 0.75/0.25 and Cl2/I2 0.75/0.25. No unusual problems were encountered for Cl3, and the final refined composition of the complex is then  $C_{16}H_{16}Cl_{2.5}I_{0.5}N_3Ni$ . The Ni–N distance in **4** (2.031(6) Å) is within the range of the corresponding pyridine-ligated system [ $\{bpa(CH_2)_2O(CH_2)_2OH\}Ni(NO_3)(NO_3)$  (bpa = *N,N*-bis(2-picolyl) amine) (2.0708(13) and 2.0765(12) Å) [25].

In addition, the cobalt analogue **5** was also characterized. The structure shows that there are two independent units, and each has the same geometry. The geometry of cobalt complex (**Fig. 2.**) is similar to that of the nickel complexes, with Co–Cl distances vary from 2.2421(13) to 2.2653(13) Å, and Co–N<sub>py</sub> distance of 2.084(3) Å, respectively. The Co–N distance in **5** (2.084(3) Å) is also within the range of the corresponding pyridine-ligated system (L)CoCl<sub>2</sub> (L = 6-(Organyl)-2-(imino)pyridyl) (2.074(3) and 2.084(4) Å) [26] (see **Fig. 3.**).

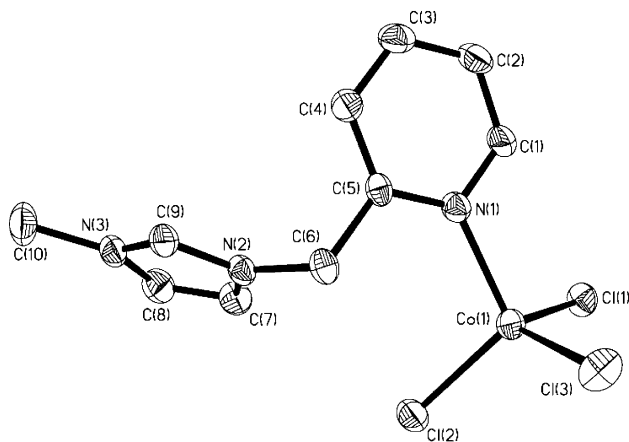


Fig. 3. Crystal structure of complex **5** (The hydrogen atoms are omitted for clarity.)

### 3.3. Ethylene polymerization

Preliminary experiments indicated that the nickel based catalyst precursor **3** and **4** can be activated for ethylene polymerization by treatment with MAO to afford Polyethylene (PE) with activities ( $10^5$  g PE mol<sup>-1</sup>Ni h<sup>-1</sup>), high molecular weight  $M_v$  ( $10^4$  g mol<sup>-1</sup>) measured by the Ubbelohde calibrated viscosimeter technique and extrapolation to the intrinsic viscosity.

Under the same condition, the complexes alone and MAO alone did not produce any polymer (run 21–23). The ethylene polymerization results are collected in **Table 3.** This data shows that complex **4** formed a catalyst with a higher activity compared to the catalyst formed by complex **3** at the same condition.

Other conditions of the polymerization reactions were also varied. Most of the variations in the conditions of polymerization were performed with catalyst **4**, the more soluble to the two catalysts studies. By increasing the Al:Ni ratio from 350:1 to 2500:1, while keeping a constant pressure and temperature, confirmed that MAO was essential for this polymerization, and the catalytic activity of complex **4** was dependant upon the Al/Ni molar ratio as shown in **Table 2** (run 1–4). The optimized Al/Ni molar ratio for the activity was 2000, and the activity decreased for both lower and higher molar ratios.

We found that the complex **4** showed the highest activity at 40 °C ( $6 \times 10^5$ ). The activity of **4** increased when the temperature of polymerization rose from 0 °C to 40 °C. This is because the concentration of active centers activated by MAO increases as the temperature is increased. At the same time it usually becomes unstable at high temperature. The highest activity at 40 °C is the result of the compromise of two factors. The decomposition rate of the active center increased and the activity dropped at 60 °C. It is clear that the  $M_v$  value was lower at higher temperature. A molecular weight of  $1.3 \times 10^5$  was obtained at a reaction time of 0 °C. Temperature also showed the similar effects on catalyst **3**.

Table 3  
Polymerization of ethylene with nickel complex **3** and **4** activated by methylaluminoxane (MAO)<sup>a</sup>

Run	Complex	Al/Ni	Pressure (atm)	T (°C)	Activity <sup>b</sup>	M <sub>v</sub> <sup>c</sup>
1	<b>3</b>	2000	1	0	3.7	18
2	<b>3</b>	2000	1	20	4.0	17.5
3	<b>3</b>	2000	1	30	4.2	16.7
4	<b>3</b>	2000	1	40	4.5	14.9
5	<b>3</b>	2000	1	60	4.1	17
6	<b>4</b>	350	1	20	0.76	–
7	<b>4</b>	1000	1	20	2.3	–
8	<b>4</b>	1500	1	20	3.7	–
9	<b>4</b>	2000	1	20	5.2	12.3
10	<b>4</b>	2500	1	20	4.3	–
11	<b>4</b>	2000	1	0	4.9	13
12	<b>4</b>	2000	1	30	5.66	9
13	<b>4</b>	2000	1	40	6.05	8.6
14	<b>4</b>	2000	1	60	5.5	11.4
15	<b>4</b>	1000	2	40	2.3	8.9
16	<b>4</b>	1000	3	40	2.4	17.2
17	<b>4</b>	1000	4	40	2.9	17.8
18	<b>4</b>	1000	5	40	3.4	17.9
19	<b>4</b>	1000	6	40	2.9	18.0
20	<b>4</b>	1000	8	40	2.75	25.0
21	<b>3</b>	–	1	20	0	0
22 <sup>d</sup>	<b>4</b>	–	1	20	0	0
23 <sup>e</sup>	–	–	1	20	0	0
24	NiCl <sub>2</sub>	2000	1	20	0	0

<sup>a</sup> Polymerization conditions: solvent, toluene; total volume, 50 ml; nickel complexes **3** and **4**, 0.4 μmol; ethylene; reaction time, 30 min.

<sup>b</sup> 10<sup>5</sup> g PE mol<sup>-1</sup>Ni h<sup>-1</sup>.

<sup>c</sup> M<sub>v</sub> (×10<sup>-4</sup> g mol<sup>-1</sup>) were measured by the Ubbelohde calibrated viscosimeter technique.

<sup>d</sup> Without cocatalyst MAO.

<sup>e</sup> Without nickel complexes but with MAO present.

Activity and molecular weights of polymers were also affected by ethylene pressure. When the ethylene pressure is lower than 5 atm, the activity of complex **4** is increasing with ethylene pressure. However, it drops obviously when the ethylene pressure is higher than 5 atm. According to Hicks et al. [27], the low activity at high ethylene pressure may partly be due to impurities in the monomer feed. On the other hand, the ethylene pressure can also affect the molecular weight of polyethylene effectively. As the ethylene pressure goes up, the molecular weight increases accordingly. In the <sup>13</sup>C NMR spectrum of polyethylene (run 4), methyl branches were identified by the resonance at 30.1 ppm(CH<sub>2</sub>), 20.1 ppm(CH<sub>3</sub>), 30.3(CH), 37.7 ppm(α-CH<sub>2</sub>), 30.5 ppm(γ-CH<sub>2</sub>), 27.6 ppm(β-CH<sub>2</sub>), which was affirmed in those entire spectrum [28]. And methyl branches were estimated as 0.37% in spectra. No other kinds of short branches can be observed through its <sup>13</sup>C NMR research.

#### 4. Conclusion

We have synthesized two mixed-halide nickel(II) complexes and one cobalt(II) complex by straightfor-

ward method. Our preliminary study shows that new nickel complexes **3**, **4** containing picolyl-functionalized imidazolium ligand show activity as catalyst precursors in ethylene polymerization.

#### 5. Supplementary data

CCDC-259451 (**2**), CCDC-259452 (**4**) and CCDC-259453 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.

#### Acknowledgements

Financial support by the National Nature Science Foundation of China for Distinguished Young Scholars (29925101, 20274008) and by the Doctoral Fund of Education Ministry of China (No. 20020246011) is gratefully acknowledged.

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