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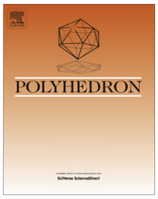

Synthesis and crystal structure determination of Mn(II) Schiff base complexes and their performance in ethene polymerization

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ABSTRACT

Mn(II) complexes **1**–**10**, of which eight are novel, were prepared in high yields by reacting $MnCl_2$ with bidentate *N*,*N*′-imine-pyridine and *N*,*N*′-imine-quinoline-type donor ligands having different kinds of chemical modifications. The complexes were fully characterized by elemental analysis, mass spectrometry and IR spectroscopy. Crystal structures of **6**, **7** and **9** were determined by X-ray crystallography and the results showed that **6** has a dimeric square-pyramidal geometry, whereas **7** and **9** have distorted octahedral structures. Magnetic studies on the high spin complexes **6** and **9** showed that the former exhibits a weak intramolecular antiferromagnetic interaction through the chloride-bridging ligands with a magnetic exchange coupling $J = -0.46(6)\ \text{cm}^{-1}$, whereas the latter, as expected for its mononuclear structure, only shows very weak intermolecular interactions and/or zero-field splitting effects. All the complexes were activated with methylaluminoxane and investigated under low pressure (5 bar) for ethene polymerization at 60 °C. Complexes **1** and **6**–**10** showed catalytic activity. The prepared polyethenes exhibited high molar masses (296 000–399 000 g/mol) and high melting temperatures (133–140 °C). The low molar mass distribution values of 2.15–2.55 indicated single-site polymerization behavior.

1. Introduction

Manganese Schiff base complexes have been extensively studied due to their catalytic [1–7], magnetic [8] and coordination properties [9]. They catalyze various reactions effectively, such as enantioselective olefin epoxidation [1], oxidation of sulfides [2], hydrocarbons [3] and alcohols [4], as well as other asymmetric reactions [5]. On the other hand, manganese catalysts in general are still rarely used in olefin polymerization, though during the past few years there has been a growing interest for their development [6,7]. Manganese complexes are interesting particularly as they are expected to have unique features differing both from early and late transition metal catalysts [6e,7a].

Manganese(II) complexes with coordinated bidentate nitrogen containing ligands and two chlorine anions have so far only been of limited interest, even though they have shown promising magnetic [10], photoluminescence [11], antibacterial and antifungal [12], and catalytic [13] properties. In our previous study $MnCl_2$ was reacted with a number of tridentate and tetradentate nitrogen containing ligands and the complexes thus obtained were further alkylated and activated with methylaluminoxane (MAO), and then studied as catalysts in ethene polymerization [6a]. As an augmentation to this work, we synthesized and fully characterized herein a series of Mn(II) complexes with bidentate Schiff base ligands bearing nitrogen donor atoms (Scheme 1). The catalytic activities of the prepared complexes were demonstrated for low pressure ethene polymerization.

2. Experimental

2.1. Materials and general procedures

All the complex preparations and polymerization experiments were performed under argon using standard Schlenk techniques or in a glove box. Solvents (HPLC grade) were dried over sodium flakes and distilled before use. Anhydrous $MnCl_2$ was purchased from Aldrich and stored under an argon atmosphere. MAO (30% in toluene) was obtained from Borealis Polymers Ltd. Other reagents of high purity grade were purchased from commercial sources and used as received.

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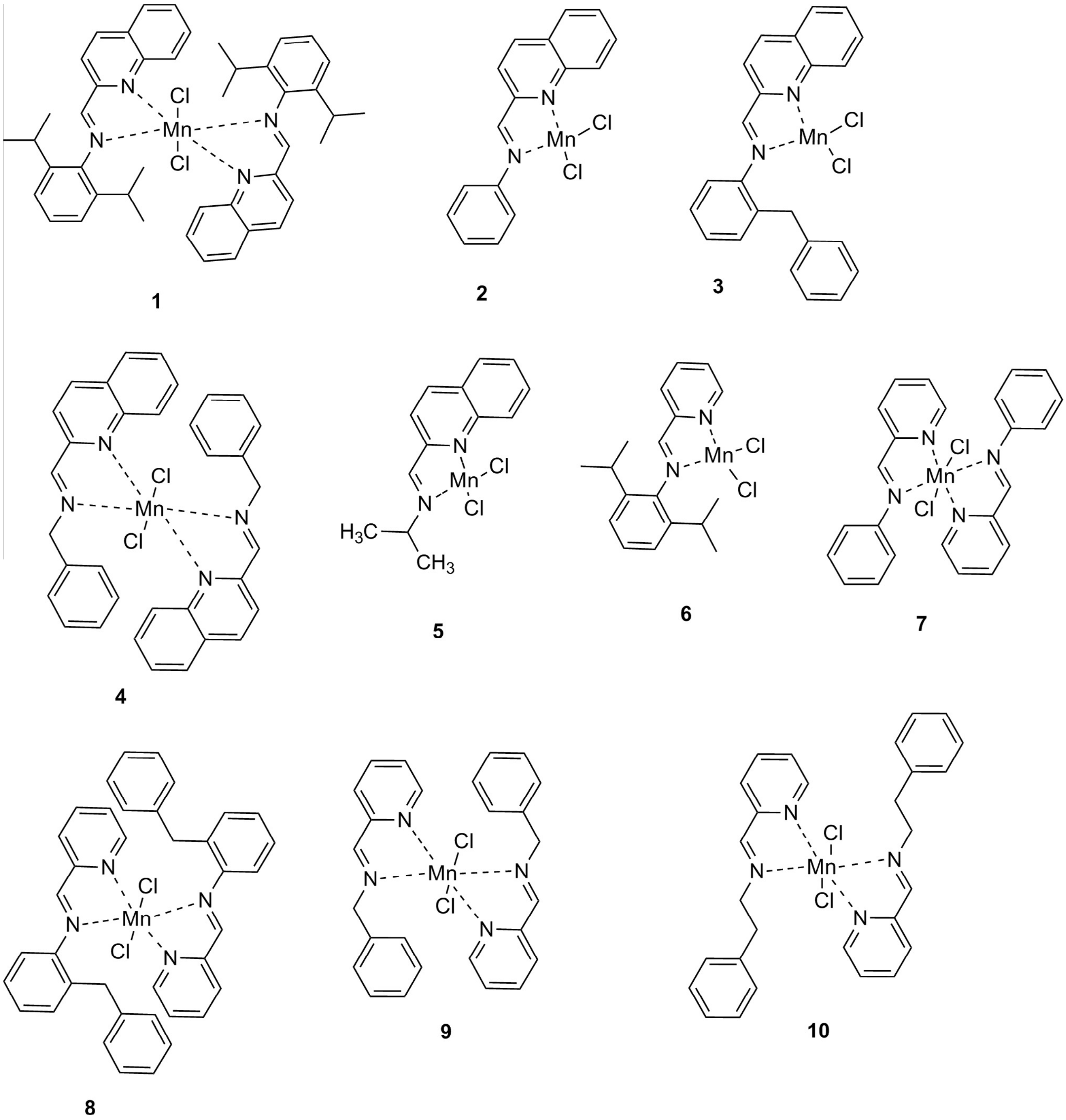
2.2. Polymerization procedure

Ethene polymerizations were done in a Büchi 1 L stainless steel reactor under Ar. The reactor was loaded with the Mn(II) complex (20 μmol), toluene (200 mL) and the cocatalyst (MAO 30%, cocatalyst:catalyst ratio 1000) and the autoclave was sealed. After loading the reactor with ethene (5.0 bar), it was kept at room temperature under stirring for 1 h, followed by overnight heating at 60 °C. More details about the experimental procedure are given elsewhere [6a].

2.3. Complex and polymer characterizations

The electrospray ionization time-of-flight (ESI-TOF) mass spectra of the complexes were recorded with a Bruker Microtof mass spectrometer and the mass spectra of the ligands were measured with a JEOL JMS-SX 102 EI$^+$ instrument (70 eV), using a direct inlet method. Infrared spectra were recorded with a Perkin–Elmer Spectrum GX apparatus and elemental analyses were performed with an EA 1110 CHNS-O CE instrument. NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Gemini 2000 spectrometer operating at 200 MHz (^{1}H NMR) and 50 MHz (^{13}C NMR). The field dependence of the magnetization at different temperatures and variable temperature (2–300 K) magnetic susceptibility measurements on polycrystalline samples of **6** and **9** were carried out with a Quantum Design SQUID MPMS XL-5 device operating at different magnetic fields. The experimental susceptibilities were corrected for the sample holder and diamagnetism of the constituent atoms using Pascal's tables.



Scheme 1. A series of synthesized Mn(II) complexes (**1**–**10**).