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Some Transition Metal Complexes Bearing Artemisinin Derivatives and (N-N-O) Tridentate Chromium (III) Complexes Ligated by 2-benzimidazo-yl-6-acetyl-pyridines for Catalytic Behaviour towards Ethylene

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Abstract: Interventions of metal complexes in the area of metallopharmaceutical and polymer sciences play a great economic importance to human challenges. Complexation behavior of some artemisinin derivatives with late transition metals and chromium-benzimidazolpyridine analogues have been investigated. The Fe(III), Zn(II) and Cd(II) complexes of artesunate and artemether and that of chromium-benzimidazolpyridine were synthesized with molar ratio of metal to ligand between 1:1 and 1:2. Structural elucidation using X-ray analysis and other characterization of the complexes (AAS, IR, UV, E.A, NMR) were carried out to explore the coordination affinity of them viz-a viz bonding, geometries and elemental composition. The IR absorption revealed that artesunate acts as monodentate specie through carbonyl group on coordination. However, its bidentate mode was also observed with carboxylic group acting as C=O and C-O bonding when deprotonation happened. Artemether (L2) was synthesized using artesunate and its structure was confirmed by single crystal X-ray crystallography as well as its Zn(II) complex exhibiting a square planar geometry. A series of 2-benzimidazolpyridine derivatives (L3-L6) and their chromium complexes were synthesized and characterized. In the presence of methylaluminoxane (MAO), all chromium complexes show good activity for ethylene oligomerization and polymerization whereas with diethylaluminium chloride (Et_2AlCl_2) the complexes show moderate activity. The distribution of oligomers obtained follows Schulz-Flory rules with high selectivity for α -olefins. The combined productivity (meaning both activities of ethylene oligomerization and polymerization) are improved with increasing ethylene pressure. The results show that the reaction conditions greatly affect the properties of the polymer such as molecular weight distribution and melting point (T_m) with extremely broad molecular weight distributions. With elevating reaction temperature from 0 to 60 °C, the melting point (T_m) of resultant polyethylene decreased rapidly from 134 °C to 70 °C.

Key words: Artemisinin, pyridine, ethylene, co-catalyst.

1. Introduction

The discovering of new bioactive drugs still remains the available drug framework as it is an attractive area for alleviating plasmodia resistance and being a new

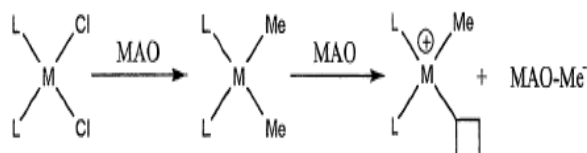
impetus to chemotherapeutic [1-3]. Coordination compounds play an essential role in life (chemotherapy) [4-8]. Complexes of sulphur drugs are potential antibacterial [9]. The transition metal complexes, however, in medicine and other biological areas as well are of great interest in the world today. Artesunate and artemether as the semi-synthetic derivative of artemisinin

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have been used for the treatment of malaria by injection [9]. In fact, the biological activity of the artemisinin (a class of sesquiterpenes lactones antimalarial drugs) has been extensively investigated [10-12], but few works on the synthesis and structural elucidation of their metal complexes have been established.

Furthermore, metal complexes are also catalyst precursors for olefin oligomerization and polymerization other applications [13]. Following the commercialization of chromium-based catalysts for the selective trimerization of ethylene to 1-hexene by the Phillips Petroleum Co. [14], there have been a number of recent reports of new highly selective chromium catalyst systems based on N-N-N [15, 16], P-N-P [17, 18] and S-N-S [19] ligands. Several others with a late transition metal are suitable to polymerize ethylene to give short chain oligomers and highly branched or linear polymers [20-22]. Various co-catalysts have been employed to activate different metal complexes for ethylene oligomerization and/or polymerization. Methylaluminoxanes (MAO) and its modified form (MMAO) are the most widely used activators [23-27]. Other activators are Lewis-acids such as ethylaluminumchloride (EtAlCl₂), diethylaluminumchloride (Et₂AlCl), triethylaluminum (Et₃Al) and combinations of triisobutylaluminum/tris (pentafluorophenyl) borane (^tBu₃Al/B(C₆F₅)₃) [16, 17].

Common to most of these co-catalysts is the formation of an active coordinative unsaturated cationic metal complex (Scheme 1). In the polymerization of ethylene, the α -olefin normally inserts rapidly into the M–Me (M=/metal) bond starting the polymerization chain. However, the choice of this co-catalyst has been shown to have significant effect not only on the catalyst activity as well as the selectivity towards



L = Ancillary ligand; M = Metal; □ = Free coordinated site

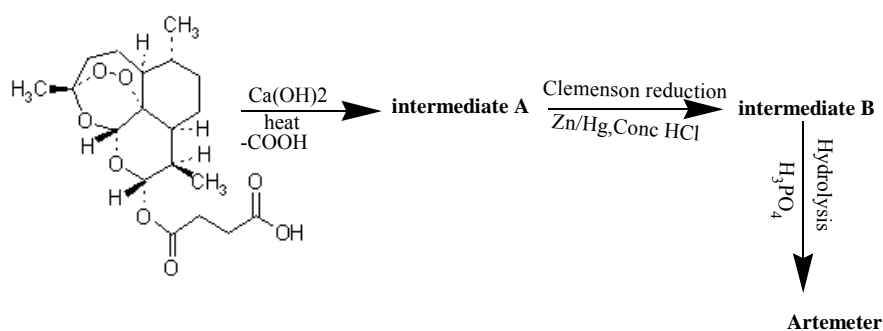
Scheme 1 Mechanism of MAO cocatalyst reaction.

oligomerization and/or polymerization [22-24].

It is seemed worthwhile to study the complexation behavior of artemisin and report newly developed 2-Benzimidazolylpyridine chromium complexes with N-N-O donor atoms with view to probe the role of the metal center with ligands derivatives for the steric and electronic effects. These compounds activated with MAO, MMAO and Et₂AlCl were investigated. In the presence of methylaluminoxane (MAO), all the chromium complexes showed high ethylene oligomerization activities and moderate polymerization activities. The influence of the reaction parameters such as pressure and reaction temperature on the catalytic behaviours was investigated.

2. Experimental Section General Considerations

All manipulations of air and/or moisture sensitive compounds were performed under nitrogen atmosphere using standard schlenk techniques. Artesunate was pharmaceutical grade (Swiss pharma). Solvents were dried by literature methods [18]. MAO, (1.46 M solution in toluene) and MMAO, (1.93 M in heptane) were purchased from Akzo Nobel Corp. Et₂AlCl (1.90 M solution in hexane) was purchased from Acros chemicals. All other reagents were purchased from Aldrich & Sigma and were directly used without further purification unless otherwise stated. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. GC analysis was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μ m film thickness) DM-1 silica capillary column. The yield of oligomers was calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated areas in the GC trace. ¹H and ¹³C NMR spectra of the PE samples were recorded on a Bruker DMX 300 MHz instrument at 110 °C in 1, 2-dichloro-



Scheme 2 Synthesis of Artemether.

benzene-*d*₄ using TMS as the internal standard.

2.1 Preparation of Artemether from Artesunate

Pure artesunate [L1] (2.5 g, 5.0 mmol) was dissolved in 10 mL acetonitrile, calcium hydroxide [0.74 g, 10.0 mmol] was added to the solution. The mixture was then refluxed for 2 h and allowed to cool to room temperature. The carbonyl group present in the material is reduced using Clemmensen reduction reagent/catalyst Zn/Hg with 5 mL of the conc. HCl acid. The product was hydrolysed with phosphoric acid and methylated with methyl iodide [0.13 mL, 2.1 mmol] while stirring vigorously for 12 h. The mixture was filtered and the filtrate was collected which was then evaporated to remove the solvent (Scheme 2).

Yield: (0.52 g, 2 mmol) 49%, M. pt: 860C, Rf: 0.36, M.F= C₁₆H₂₆O₅; M. wt: 298 g.mol⁻¹.

IR (KBr, cm⁻¹) 3454.63, 2845.10, 1450, 1374, 1106.

UV-Vis (methanol): λ_{max}, 226 nm; Conductivity: 5.106×10⁻³ Ω⁻¹cm⁻¹.

2.2 Synthesis of Fe-Artesunate Complex

A mixture of Artesunate (L1) (0.768 g, 2.0 mmol) and FeCl₃.6H₂O (0.54 g, 2.0 mmol) in freshly distilled 20 mL methanol was refluxed for 12 h. The light brown colour of the solution changed to dark-brown with no precipitate formation after 24 h constant stirring. The reaction mixture was filtered. The mixture was placed in an ice bath overnight followed by slow evaporation for 2 weeks. The solid product obtained was washed with diethyl ether and dried *in vacuo*.

Yield: (0.77 g, 1.5 mmol) 73%, M.wt: 530, M.pt

(decp.at temp)>250°C, Anal. Calcd. for C₁₉H₂₈O₈Fe₂ClH₂O,: C, 43.02; H, 5.66; Fe, 6.26; Found: C, 43.05; H, 5.50.

IR(KBr,cm⁻¹) : 3437, 2924,1735,1457,1370,1319.

UV-Vis (methanol) λ, nm: 259, 352; Conductivity: 1.60 × 10⁻¹ Ω⁻¹cm⁻¹.

2.3 Synthesis of Zn-Artesunate Complex

A mixture of Artesunate (L1) (0.384 g, 1.0 mmol) and ZnSO₄.7H₂O (0.575 g, 2.0 mmol) in freshly distilled 20 mL methanol was stirred for 6 h at room temperature. 5mL of 0.1M NaOH was also added to deprotonate the ligand for more coordination. The colourless solution yielded precipitate after 1 h. The reaction mixture was further concentrated at low temperature and then filtered. The white residue was washed with diethylether and recrystallised with CH₂Cl₂/hexane.

Yield: (0.22 g, 0.42 mmol) 42% M. wt: 521, M.pt (decp. at temp > 179 °C

anal. calcd. for C₁₉H₂₈O₈Zn4H₂O C, 43.76; H, 6.91 Zn, 5.0 Found: C, 43.97; H, 6.60.

IR (KBr, cm⁻¹): 3385, 1695, 1377, 1308.

UV-Vis (methanol) λ, nm: 229; Conductivity: 9.176×10⁻⁴ Ω⁻¹cm⁻¹.

2.4 Synthesis of Cd-Artesunate Complex

A mixture of Artesunate (L1) (0.768 g, 2 mmol) and CdCl₂.21/2H₂O (0.251 g, 1.1 mmol) in freshly distilled 20 mL methanol was stirred for 4 h at room temperature. The colourless solution yielded precipitate after 3 h. The reaction mixture was further

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concentrated in an ice bath overnight. The mixture was filtered. The residue was washed with diethylether and dried *in vacuo*.

Yield: (0.60 g, 1.1 mmol) 53% M.wt: 567 M.pt: (decp. at temp) $>$ 198 °C

anal. calcd. for $C_{19}H_{28}O_8Cd_2Cl$ C,40.21; H,4.94 Found:C,40.27; H,4.92.

NMR 2H, CH₂, (1.0); H, O-CH (5.0).

IR (KBr, cm⁻¹): 3528,2953,1374,1323.

UV-Vis (methanol) λ , nm: 262.

Conductivity: $5.106 \times 10^{-1} \Omega^{-1}cm^{-1}$.

2.5 Synthesis of Zn Complex of Artemether

A mixture of Artemether (L2) (0.894 g, 3.0 mmol) and ZnSO₄.7H₂O (0.270 g, 2.0 mmol) in freshly distilled 20 mL ethanol was refluxed. The solution was colourless with no precipitate formation after 6 h continuous stirring. The reaction mixture was cooled in ice bath, concentrated and the filtrate was left to undergo slow evaporation, the white crystal formed after 3 weeks, which was washed with diethylether and dried *in vacuo* gave X-ray Crystallographic measurements (Table 1).

Yield: (0.59 g, 1.45 mmol) 45%, M.wt: 435 M.pt: (decp. at temp) $>$ 240 °C

anal. calcd. for $C_{16}H_{26}O_5Zn4H_2O$ C,42.38; H,7.51 Found:C,41.70; H,7.23.

IR(KBr, cm⁻¹): 3448, 2845,1451,1012.

UV-Vis (methanol) λ , nm: 223.

Conductivity: $9.176 \times 10^{-2} \Omega^{-1}cm^{-1}$.

2.6 Preparation of the Chromium Complexes with Precursor Compounds

All the organic compounds used as ligands for the chromium complexes (C5-C7) were prepared by employing the previously reported procedure [19, 21]. A 0.20 mmol of respective 2-Benzimidazolylpyridine ligand were dissolved in 10 mL of freshly distilled CH₂Cl₂ in a schlenk tube. Then 0.20 mmol CrCl₃ (THF)₃ was added under nitrogen atmosphere. The reaction mixture was stirred for 12 h after which the

Table 1 Crystal data structure refinement of Artermether.

$C_{16}H_{26}O_5$	$D_x = 1.274 \text{ Mg m}^{-3}$
$M_r = 298.37$	Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, $P2_12_12_1$	Cell parameters from 7832 reflections
$a = 10.315 (2) \text{ \AA}$	$\theta = 2.4\text{--}29.3^\circ$
$b = 13.620 (3) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 11.073 (2) \text{ \AA}$	$T = 103 \text{ K}$
$V = 1555.6 (5) \text{ \AA}^3$	Chunk, colorless
$Z = 4$	$0.84 \times 0.47 \times 0.34 \text{ mm}$
$F_{000} = 648$	

solvent volume was reduced *in vacuo*. Diethyl ether was then added to precipitate the complex and allowed to stand for 30 minutes. The supernatant was removed and the precipitate was washed with diethyl ether several times and dried *in vacuo*.

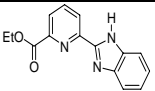
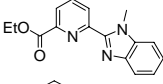
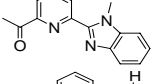
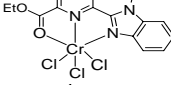
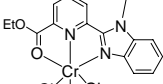
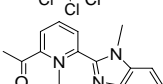
The complexes were obtained green crystalline powders. Yields: C5, 84.9%; C6, 88.5%; C7, 97%. The complexes were identified by infrared spectrometry (Table 2). The synthesized complexes did not show a melting point under inert atmosphere but decomposition at higher temperatures. Decomposition temperatures: C5, 240 °C; C6, 250 °C; C7, 210 °C.

The chromium complexes were characterized with IR and elemental analyses: C5 IR (KBr, cm⁻¹): 3068 ($\nu_{N=H}$), ($\nu_{C=O}$), 1720, 1662, 770; C = 42.73% ($C_{\text{calc.}} = 42.33\%$), H = 3.25% ($C_{\text{calc.}} = 3.08\%$), N = 10.1% ($C_{\text{calc.}} = 9.87\%$); C6, ($\nu_{C=O}$), 1730, 1586, 1472, 759. C = 43.27% ($C_{\text{calc.}} = 43.71\%$), H = 3.53% ($C_{\text{calc.}} = 3.44\%$), N = 9.79% ($C_{\text{calc.}} = 9.56\%$); C7, ($\nu_{C=O}$), 1704, 1587, 1465, 690. C = 44.12% ($C_{\text{calc.}} = 43.98\%$), H = 3.78% ($C_{\text{calc.}} = 3.91\%$), N = 10.15% ($C_{\text{calc.}} = 10.26\%$).

2.7 Procedure for Homogenous Ethylene Oligomerization and Polymerization

The catalyst precursor (chromium complex) was dissolved in toluene in a Schlenk tube stirred with a magnetic stirrer under an ethylene atmosphere (1 atm), and the reaction temperature was controlled by a water bath. The reaction was initiated by adding the required amount of co-catalyst. After the desired period of time, a small amount of the reaction solution was collected with a syringe and was quenched by the addition of 5%

Table 2 Infrared Spectral Data of the ligand derivatives [20] and Chromium complexes C1-C3 (cm⁻¹).

Compound	$\nu(\text{C=O})$	$\nu(\text{N-H})$	$\nu(\text{C=N})$	Pyridyl ring stretch
	1719s	3054br	1593w	1459m
	1730s		1586w	1472m
	1704s		1587w	1465m
	1642s	3064br	1599w	1469m
	1641s		1595w	1469m
	1703s		1595w	1486m

s = strong; m = medium; w = weak; br= broad.

aqueous HCl. An analysis by gas chromatography (GC) was carried out to determine the distribution of oligomers obtained. The remaining solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was collected by filtration, washed with ethanol, dried under vacuum at 60 °C to constant weight, weighed, and finally characterized. The reactions at higher ethylene pressure were however carried out in a 250 mL stainless steel autoclave reactor equipped with a mechanical stirrer and a temperature controller. The desired amount of MAO, a toluene solution of the chromium complex (30 mL), and toluene (70 mL) were added to the reactor in this order under an ethylene atmosphere. When the reaction temperature was achieved, ethylene at the desired pressure (20 atm) was introduced to start the reaction. After 1 h, the reaction was stopped and further analysis of oligomers and polymers was carried out as above.

3. Results and Discussion

The reaction of different transition metal salts with artesunate and artemether in methanol produced

crystal. Iron and zinc sulphates formed complexes of artesunate at elevated temperature. Except for cadmium complex that was synthesized in 1:2 and zinc complex 2:1 metal to ligand mole ratios, iron was prepared in 1:1 stoichiometric ratio with good to excellent yields. The molecular structure of artermether is shown below and selected bond length, bond angles and atomic coordinates for non hydrogen atoms are given (Fig. 1).

The elemental analysis results of the complexes are in good agreement with the formula. The complexes were insoluble in common organic solvents. All the complexes are soluble in DMSO. Most of the metal complexes decompose at temperatures greater than that of the ligand. The molar conductance values measured

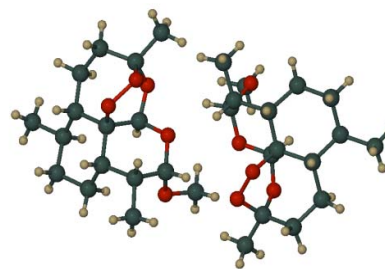


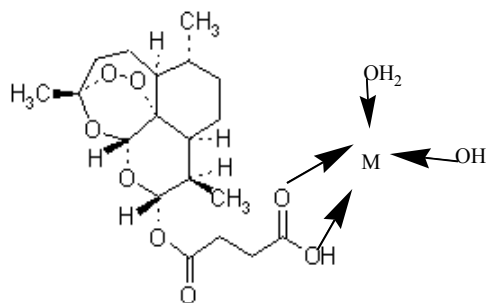
Fig. 1 The two crystallographically independent molecules of artemether.

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in methanol (10^{-3}) for the complexes are in $1.184 \times 10^2 - 7.55 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ range. As expected no extra bands in d-d were observed for Cd(II) and Zn(II) complexes due to 1S (no splitting) spectroscopic term. Fe (III) is a moderately oxidizing ions and many of its complexes exhibit $n-\pi^*$ and ligand to metal charge transfer transition (L-MCT) for the complex. The ligand artesunate shows absorption at 3437 cm^{-1} for O-H carboxylic acid with moderate and broad intensity; while 1457 cm^{-1} and 1370 cm^{-1} for out of plane bending vibration O-H. 2845 cm^{-1} band is attributed to C-H str. alkane bond. 1735 cm^{-1} (C=O str. for ester), 1646 cm^{-1} (C=C str. aromatic), 1319 cm^{-1} (C-O str). All these are characteristics of the ligand. From the IR data complexes, the functional groups indicated in the ligands are also present in the complexes, but 3443 cm^{-1} and 1706 cm^{-1} of the Fe(III) complex mark the difference compared to that of ligand. The broad band (O-H) ν 3437 cm^{-1} has disappeared and ν (C=O) bond weaken in the complex region. Therefore, artesunate coordinates through the C=O. This observation is common to all other complexes with C=O band which shifts to lower frequencies or some disappeared while ν O-H shifted to higher frequency upon complexation (Fig. 2).

3.1 Synthesis and Characterization of Chromium Complexes

The chromium complexes were synthesized by an equimolar reactions of the synthesized 2-benzimidazopyridine derivatives with $\text{CrCl}_3(\text{THF})_3$ in CH_2Cl_2



Where M = Fe

Fig. 2 Proposed structure of Iron-Artesunate complex.

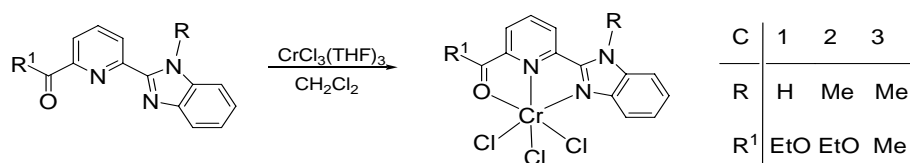
(Scheme 3).

The reaction starts immediately and can be observed by a color change of the reaction mixture from purple to green. The yields of the complexes are almost quantitative. Due to the paramagnetic nature of this type of complexes [21], it is not very informative to characterize them by NMR spectroscopy. The infra red spectrometric analysis revealed that absorption bands of complexes were shifted when compared with the IR spectrometry of free organic compounds (Table 2).

According to their IR spectra, the typical stretching frequency of $\nu(\text{N-H})$ shift to a band at around 3064 cm^{-1} for C1, and the frequencies of ν (C=O) red shift to bands between 1641 and 1646 cm^{-1} an indication of coordination through carbonyl oxygen, while $\nu(\text{C=N})$ shifts to higher bands between 1595 and 1599 cm^{-1} (C5-C7). On the other hand, the strong ligand bands at around 1325 cm^{-1} in the ligand shift to higher frequencies around 1343 cm^{-1} , indicating coordination through the pyridine nitrogen. All of the complexes were consistent with their elemental analyses.

3.2 Ethylene Oligomerization and Polymerization

The effects of various co-catalysts at different Al/Cr ration on the productivity for ethylene reactivity were first studied in detail with C1, and the results are shown in Table 3. The results indicate that the ethylene reactivity is strongly influenced by the chosen co-catalysts as well as co-catalyst/Cr ratio. The C1/MAO system shows remarkably higher catalytic activity than the other systems activated with MMAO and Et_2AlCl at all ratios, however the peak activity is observed at Al/Cr ratio of 1000/1. The lower activity with MMAO could be traced to the presence of triisobutylaluminumoxane (TIBAO), and the species generated therefrom hinder the insertion reaction of ethylene, due to their steric bulkiness [26]. The products obtained by C5-C7 with all the co-catalysts comprised of oligomers and waxlike polyethylene. However complexeC1/MAO with the highest performance in the series (Entry 3, Table 3) produced



Scheme 3 Synthesis of Chromium complexes (C5-C7).

Table 3 Result of ethylene oligomerization/polymerization of Cr complexes (C1-C3)/MAO, MMAO and Et₂AlCl.

Entry	Complex	Co-cat	Al/Cr	Oligomer		Polymer	
				Activity ^b	Distribution ^c	Activity ^b	% PE (wt %)
1	C5	MAO	200	0.78	C4, C6	Trace	-
2	C5	MAO	500	4.14	C4-C8	Trace	-
3	C5	MAO	1000	8.70	C4-C20		74.1
4	C5	MAO	1500	7.15	C4-C8		24.7
5	C5	MMAO	200	1.18	C4	Trace	-
6	C5	MMAO	500	5.28	C4	Trace	-
7	C5	MMAO	1000	5.63	C4		62.0
8	C5	MMAO	1500	3.17	C4, C6		45.8
9	C5	Et ₂ AlCl	200	0.21	C4-C16	Nd	-
10	C5	Et ₂ AlCl	500	4.43	C4-C18	Nd	-
11	C5	Et ₂ AlCl	1000	6.71	C4-C20		10.5
12	C5	Et ₂ AlCl	1500	7.15	C4-C16	Trace	-
13	C6	MAO	1000	5.34	C4, C6		66.7
14	C7	MAO	1000	7.65	C4, C6		59.0
15	C6	MMAO	1000	2.92	C4-C8		54.2
16	C7	MMAO	1000	3.41	C4		49.5
17	C6	Et ₂ AlCl	1000	7.76	C4, C6		14.1
18	C7	Et ₂ AlCl	1000	8.16	C4		8.5
19 ^d	C5	MAO	1000	47.1	C4-C20		75.6
20 ^e	C5	MAO	1000	13.6	C4-C8		70.1
21 ^f	C5	MAO	1000	61.5	C4-C20	7.64	90.1

^aGeneral conditions: 5 μmol of complex; ethylene pressure 1 atm; temperature 20 °C; 1h; 30 mL Toluene as solvent. ^bIn units of 10⁴ g (mol of Cr)⁻¹h⁻¹. ^cDetermined by GC and GC-MS. ^dTemperature 40 °C. ^eTemperature 60 °C. ^fEthylene pressure 20 atm.

almost all isomers that are possible for olefins with even carbon number.

The ethylene reactivity greatly depends on the ligand environment. It is observed that for the same reaction conditions, the productivity decreased in the orders C5 > C6 > C7 with MAO and MMAO co-catalyst and C7 > C6 > C5 with Et₂AlCl (Fig. 3). This result can be attributed to the deprotonation of N-H group to give anionic amide ligands when activated by co-catalyst of organoaluminum to form N-Al species to increase their catalytic activity. On the other hand, the incorporation of an alkyl group on the N atom of imidazole into the complexes leads to a dramatic decrease in ethylene reactivity and greatly affects the distribution of the oligomers [25] (Entries 15, 21 and 22, Table 3).

As shown in Fig. 4 the complexes C5-C7/Et₂AlCl showed lowest activity than C5-C7/MMAO which in

turn lower than C5-C7/MAO in their polymer yields. It can therefore be argued that stability of the active centre for polymerization is a function of the organoaluminium type. β-Hydrogen transfer is more favored with the Et₂AlCl co-catalyst, thereby supporting the formation of oligomers. However, with other co-catalysts, chain elongation is favored relative to chain transfer. The influences of the reaction temperature and pressure on ethylene activation were investigated in detail with C5. Elevating the reaction temperature from 0 to 60 °C, the combined catalytic reactions of oligomerization and polymerization doubled in ten folds (Entry 23, Table 3). The melting point (T_m) of resultant polyethylene decreased rapidly from 134 °C to 70 °C and molecular weight from 10.6×10⁴ to 0.1×10⁴. Increased catalytic activities were also observed by elevating ethylene pressure from 10 to

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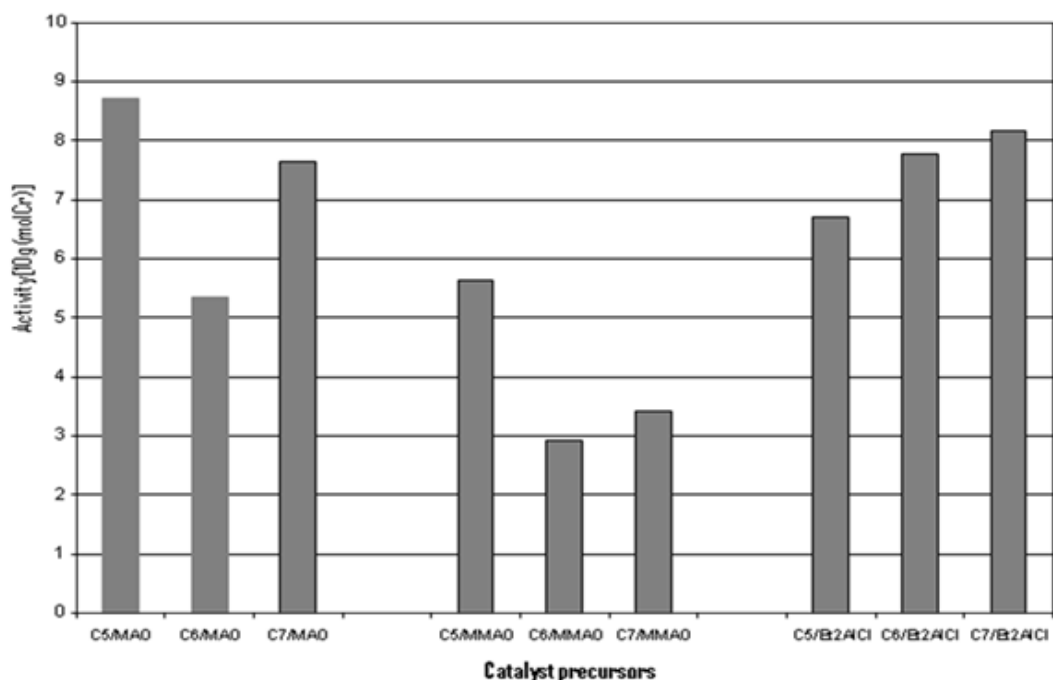


Fig. 3 Comparison of the observed activities of the Cr-complexes (C5-C7) activated by various co-catalyst.

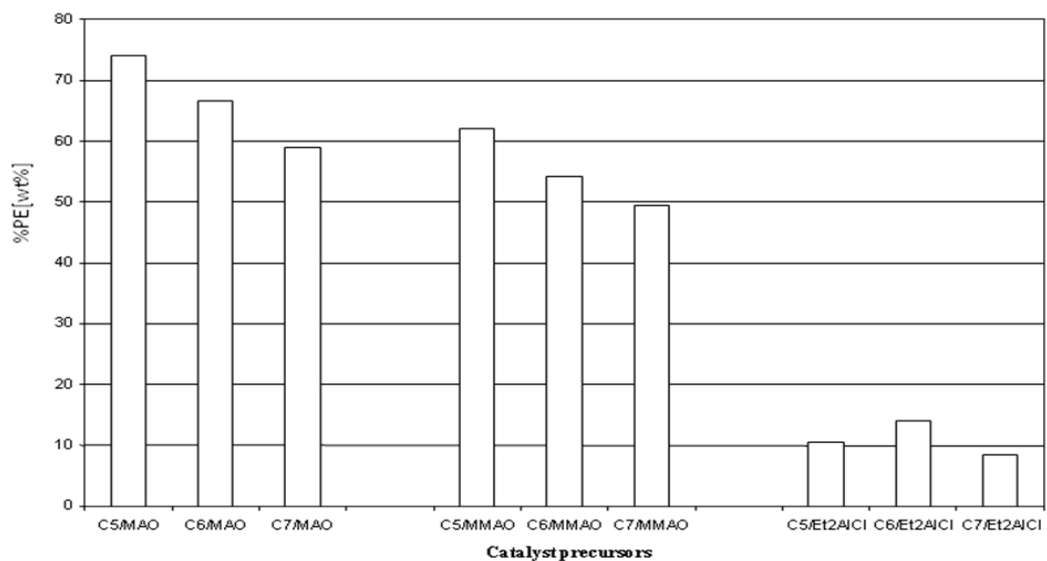


Fig. 4 Comparison of the %PE obtained with Cr-complexes (C5-C7) activated by various co-catalyst.

20 atm (Entry 25, Table 3).

4. Conclusion

Artemether was synthesized as potential ligands in appreciable yields and characterized by single crystal X-ray crystallography. New metal-drug complexes were synthesized with artesunate acting as mono/bidentate ligand through C=O (ester

group)/carboxylic group depending on pH medium resulting into tetra/octahedral coordinated compounds.

With MAO as the co-catalyst, the chromium (III) complexes show high activity for both oligomerization and polymerization of ethylene. The complexes with N-alkyl substituent show lower activity than the complexes with N-H when activated with either MAO or MMAO. Activation with Et₂AlCl gave a catalyst

with moderate activities for oligomerization and little or no effect for ethylene polymerization. Increase in reaction temperature and pressure have great effects on activities as well as polymer properties.

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