



Characterisation of magnesium carboxylates and their catalytic C–C bond formation reactions

Bikash K. Dey, Anirban Karmakar, Jubaraj B. Baruah*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039 Assam, India

ARTICLE INFO

Article history:

Received 3 October 2008
Received in revised form 9 January 2009
Accepted 12 January 2009
Available online 20 January 2009

Keywords:

Magnesium carboxylates
Catalyst
C–C bond formation

ABSTRACT

Condensation reactions of aromatic aldehydes with acetone for carbon–carbon bond formation are catalysed by magnesium carboxylate complexes. Two magnesium complexes having compositions $[(4\text{-NO}_2\text{-C}_6\text{H}_4\text{CO}_2)_2\text{Mg}(\text{CH}_3\text{OH})_4]$ (**1**) and $[(4\text{-CH}_3\text{-C}_6\text{H}_4\text{CO}_2)_2\text{Mg}(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2]$ (**2**) that are catalysts for such reactions are synthesized. They are prepared by reacting metallic magnesium with methanol in the presence of 4-nitrobenzoic acid and 4-methylbenzoic acid, respectively. Structures of **1** and **2** are determined by X-ray crystallography. The catalytic reactions of these two complexes for carbon–carbon bond formation reactions of various aromatic aldehydes with acetone are presented.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Magnesium compounds are used as mediators or catalysts for several organic reactions [1,2]. Magnesium carboxylate complexes also act as carrier for carbon dioxide [3]. Among various magnesium compounds, magnesium oxide is a versatile catalyst for carbon–carbon bond formation reactions [4–13]. The carbon–carbon bond formation by magnesium carboxylate complexes are not studied in details due to their limited synthetic procedure and hygroscopicity. It is reported that acidity of water molecules bound to magnesium ions differs in different magnesium carboxylate complexes [14]. It is also known that magnesium oxide behaves as a mild base and it can deprotonate methanol [15]. The structural aspects of magnesium carboxylate complexes are extensively studied [16–19,20] and a variety of magnesium carboxylate complexes having different structural features contribute to enzyme activities [21]. Thus, it is important to understand the structural features along with the catalytic abilities of different magnesium carboxylate complexes. In this report we describe a method for preparation of two magnesium carboxylate complexes and also report their catalytic activity for aldol condensation reactions.

2. Experimental

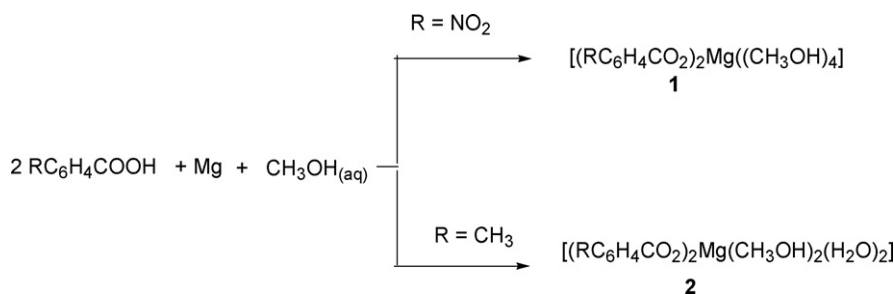
2.1. Synthesis of magnesium carboxylate complexes **1** and **2**

Metallic magnesium powder (24 mg, 1 mmol) was suspended in methanol (15 ml) with corresponding aromatic carboxylic acid (2 mmol). The mixture was refluxed for about 12 h. During this period all the metallic magnesium got dissolved and a transparent solution was obtained. Crystalline product of the magnesium complexes were obtained on slow evaporation of solvent (yield, 30–40%). The magnesium content in these complexes was determined by titration with ethylenediamine tetra-acetic acid and found to be satisfactory for the proposed structures. The complexes **1** and **2** have ^1H NMR signals identical to the parent carboxylic acid in DMSO- d_6 .

2.2. Spectroscopic data for the complexes **1** and **2**

$[(4\text{-NO}_2\text{-C}_6\text{H}_4\text{CO}_2)_2\text{Mg}(\text{CH}_3\text{OH})_4]$ (**1**): IR (KBr, cm^{-1}): 3466 (bs), 1622 (s), 1586 (s), 1507 (s), 1416 (s), 1348 (s), 1322 (s), 1107 (s), 879 (s), 799 (s), 724 (s). Crystallographic parameters: CCDC number 677166, Formula, $\text{C}_{18}\text{H}_{24}\text{MgN}_2\text{O}_{12}$, Mol. wt. 484.70, Crystal system, Monoclinic; Space group, $\text{P}2(1)/c$; $a/\text{Å}$, 12.2754(10); $b/\text{Å}$, 13.2020(10); $c/\text{Å}$, 7.3074(6); $\alpha/^\circ$, 90.00; $\beta/^\circ$, 96.064(5); $\gamma/^\circ$, 90.00; $V/\text{Å}^3$, 1177.61(16); $Z=2$; Density/ mg m^{-3} , 1.367; Abs. Coeff./ mm^{-1} , 0.139; Abs. correction, none; $F(000)$, 508; Total no. of reflections, 11319; Reflections, $I > 2\sigma(I)$, 1617; Max. $\theta/^\circ$, 28.36; Completeness to 2θ (%), 97.1; Data/restraints/parameters, 2859/0/161; Goof (F^2), 1.165; R indices [$I > 2\sigma(I)$], 0.0452; R indices (all data), 0.0870.

* Corresponding author. Tel.: +91 361 2582311; fax: +91 361 2690762.
E-mail address: juba@iitg.ernet.in (J.B. Baruah).



Scheme 1. Reactions of magnesium with methanol in the presence of aromatic acids.

[[4-CH₃-C₆H₄CO₂]₂Mg(CH₃OH)₂(H₂O)₂] (**2**): IR (KBr, cm⁻¹): 3445 (bs), 1607 (s), 1591(s), 1548 (s), 1434 (s), 773 (s). Crystallographic parameters: CCDC no. 682865; Formula, C₁₈H₂₆MgO₈; Mol. wt. 394.7; Crystal system, Monoclinic; Space group, P2(1)/c; *a*/Å, 13.5869(2); *b*/Å, 7.64960(10); *c*/Å, 10.4735(2); α /°, 90.00; β /°, 102.3940(10); γ /°, 90.00; *V*/Å³, 1346.92(9); *Z*=2; Density/mg m⁻³, 1.233; Abs. coeff./mm⁻¹, 0.122; Abs. correction, none; *F*(000), 420; Total no. of reflections, 14,242; Reflections, *I* > 2σ(*I*), 2046; Max. θ /°, 28.30; Completeness to 2θ (%), 99.4; Data/restraints/parameters, 2627/0/138; Goof (*F*²), 1.058; *R* indices [*I* > 2σ(*I*)], 0.0405; *R* indices (all data), 0.0511.

2.3. Magnesium carboxylate catalysed carbon–carbon bond formation reactions

In a typical experiment, a solution of magnesium complex **1** (5 mg, ~0.01 mmol) and acetone (580 mg, 10 mmol) in dry tetrahydrofuran (5 ml) were taken in a two necked round bottomed flask. The flask was fitted with a dropping funnel and a guard tube. It was then placed in an ice-bath maintaining temperature 5–10 °C. To this solution 4-methylbenzaldehyde (120 mg, 1 mmol) was added and

the reaction mixture was stirred for 10 h. The reaction mixture was brought to room temperature and the solvent was removed under reduced pressure. Water (5 ml) was added to the crude products and organic products were extracted with dichloromethane and dried over anhydrous sodium sulphate. The dichloromethane was removed. The residue was purified by preparative TLC. The products were further characterised by recording their ¹H NMR, IR and comparing them with authentic samples.

3. Results and discussion

3.1. Synthesis and characterization of the catalysts

The magnesium complexes **1** and **2** having composition [(4-NO₂-C₆H₄CO₂)₂Mg(CH₃OH)₄] (**1**), [(4-CH₃-C₆H₄CO₂)₂Mg(CH₃OH)₂(H₂O)₂] (**2**), were prepared by reacting of metallic magnesium with methanol in the presence of 4-nitrobenzoic acid and 4-methylbenzoic acid respectively (Scheme 1). In this reaction at first magnesium forms methoxides which reacts with carboxylic acids to give the desired metal complexes. The complexes were characterised by ¹H NMR, IR and also by determining their crystal

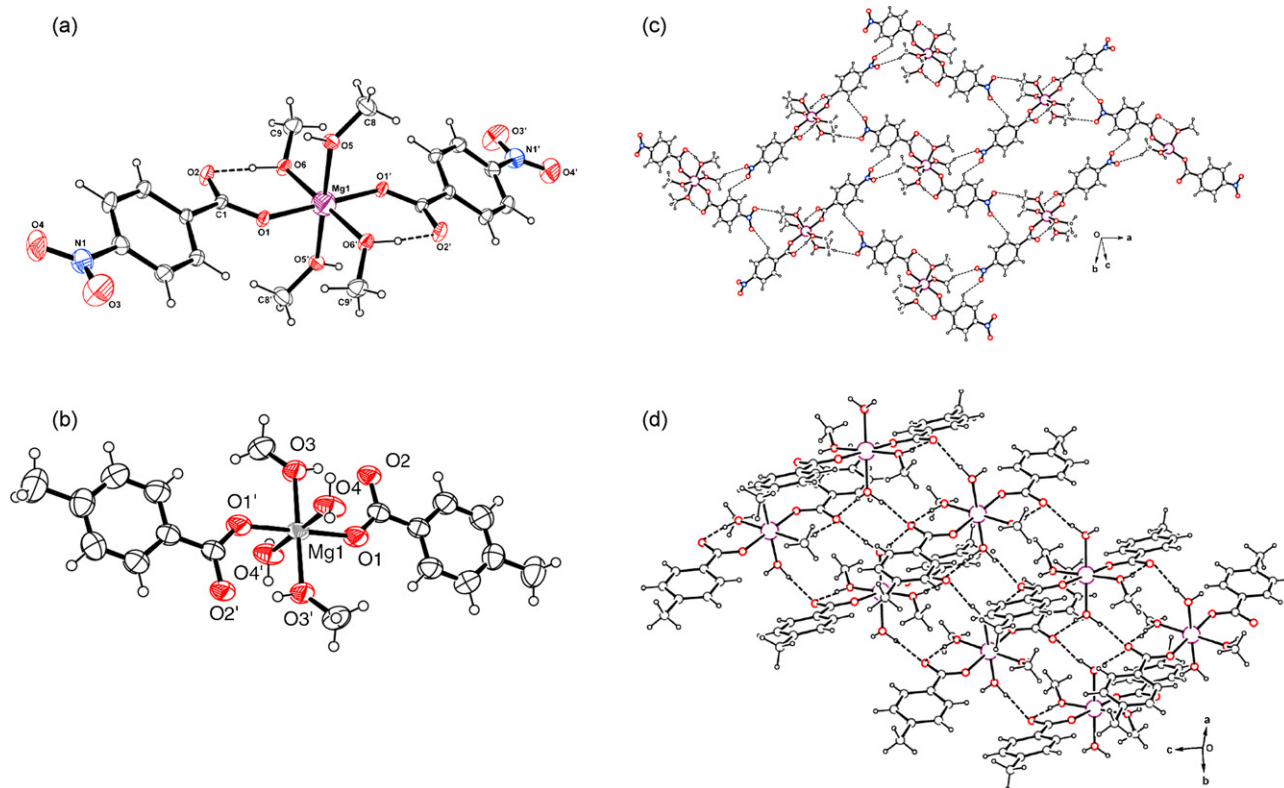


Figure 1. Crystal structure of magnesium complexes (a) **1**, (b) **2** (drawn with 50% thermal ellipsoids) and (c) and (d) are hydrogen bonded self-assemblies of **1** and **2**.

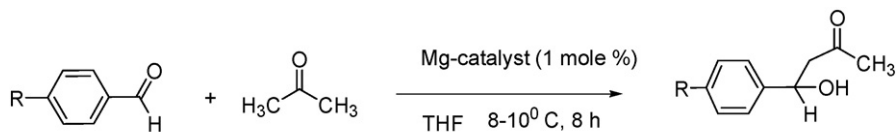
structures. The ^1H NMR spectra of these complexes shows identical signals to that of the parent carboxylic acids. Both the compounds have characteristic OH frequency in the region of $3400\text{--}3450\text{ cm}^{-1}$.

The complexes **1** and **2** have six co-ordination environment around magnesium. The complex **1** has two mono-dentate carboxylate ligands, trans to each other and the other four co-ordination sites are occupied by methanol molecules (Fig. 1a). The O–H bond of methanol molecules is involved in intra ($O_6\text{--H}\cdots O_2$; $d_{\text{D--H}}$ 1.00 Å, $d_{\text{D--A,intra}}$ 2.67 Å; $\angle\text{D--H}\cdots\text{A}$ 162.49°) as well as intermolecular ($O_5\text{--H}\cdots O_2$; $d_{\text{D--H}}$ 0.81 Å, $d_{\text{D--A,inter}}$ 2.66 Å; $\angle\text{D--H}\cdots\text{A}$ 158.53°) hydrogen bond interactions. In addition to these, the nitro groups are involved in C–H \cdots O interactions, which leads to the closed packed structures as illustrated in Fig. 1c. The packing pattern of complex **1** is controlled by N–O \cdots H interactions between the nitro groups of aromatic ring with methanol ligands (Fig. 1c) and it has a grid like structure.

In contrast to these the complex **2** has two aqua ligands, two methanol ligands as well as two monodentate 4-methylbenzoate ligands. The complex is symmetric with respect to a mirror plane and has identical pairs of ligands positioned at trans position with respect to each other (Fig. 1b). The alcohol OH groups are intramolecular hydrogen bonded ($O_3\text{--H}\cdots O_2$; $d_{\text{D--H}}$ 0.85 Å, $d_{\text{D--A,intra}}$ 2.63 Å; $\angle\text{D--H}\cdots\text{A}$ 164.86°) and the aqua ligands are involved in intermolecular hydrogen bond ($O_4\text{--H}\cdots O_2$; $d_{\text{D--H}}$ 0.85 Å, $d_{\text{D--A,inter}}$ 2.77 Å; $\angle\text{D--H}\cdots\text{A}$ 185.39°) to generate step-like structures (Fig. 1d).

3.2. Catalytic C–C bond formation reactions

The C–C bond formation reactions between aromatic aldehyde and acetone are catalysed by the magnesium complexes **1** and **2**. Both the complexes have similar catalytic efficiency. Some reactions carried out using these catalysts are shown in Equation 1. The yield of the corresponding condensed products varies from 30% to 60%. The two catalysts studied have different compositions but they show similar reactivity. Both the complexes are found to be hygroscopic and lose carboxylate as carboxylic acid by hydrolysis. The advantage of these catalytic carbon–carbon bond formation reactions is that, the products do not undergo further dehydration to form unsaturated carbonyl compounds, which is generally observed.



R = NO₂, CH₃, CH₃O, Mg-catalyst = **1**, **2**

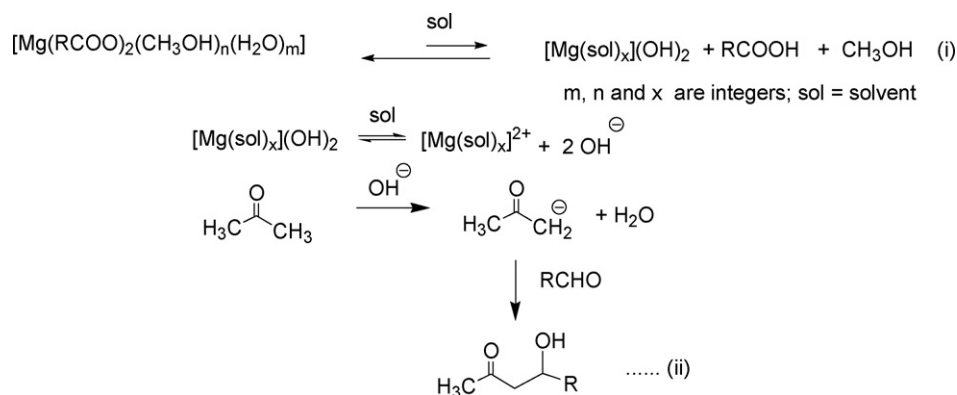
The presence of electron withdrawing groups such as nitro-group does not significantly affect the yield of the condensed product in the catalytic reactions of **1** (Table 1). But the reactions of substrates like 2-hydroxy or 4-hydroxybenzaldehyde gave very poor yield (<5% after one day continuous stirring) of condensed products. The reaction described in Equation 1 takes place at low temperature 5–15 °C in a smooth manner. Upon increasing the temperature to room temperature, the yield of condensed products does not increase. Thus, these reactions may be governed by a solvolytic equilibrium as illustrated in step (i) of Scheme 2. Such equilibrium leads to the formation of solvated magnesium hydroxides and the solvated magnesium hydroxide formed in the reaction facilitates the coupling reactions to form aldol products as illustrated in step (ii). In this step water is generated and the equilibrium of step (i) is pushed towards left side. The magnesium carboxylates thus formed are unstable and hydrolytically cleaves to give magnesium hydroxide. The process continues and makes the reaction

Table 1
Reactions of various aromatic aldehydes and acetone catalysed by **1** (1 mole %).

Entry	Aldehyde	Time (h)	Product	Yield (%)
1		12		65
2		12		60
3		12		65
4		18		55
5		18		50

catalytic. The pH of the solution remains within 7.5–8 during the course of these reactions; this suggests that the reactions take place under near neutral condition. This happens as hydrolytic cleavage of the carboxylate complexes as illustrated in the first step of Scheme 2 leads to a minimum amount of hydroxyl anion.

From the substrates shown in Table 1, moderate yield of the condensed products were obtained. The magnesium oxide nanoparticles were studied for catalytic reactions for aldol condensation [10]. Significantly, such reactions were used to prepare enantiomers in the presence of various chiral amines [22]. We studied the reaction of 4-methylbenzaldehyde with acetone in the presence of catalytic amount of **1** and amines like pyridine, triethylamine, ethylamine etc. The presence of amine in our reaction solutions led to multiple products without increase in yield of aldol products. Formation of multiple products makes the separation process very cumbersome and hence we did not proceed for further reactions with chiral amines. The reactions carried out by magnesium complexes **1** and **2** are comparable to the reported magnesium-oxide catalysed heterogeneous reactions, in terms of yields [7]; but not in terms of the stereochemistry. In the case of nano-catalysis and solid-state reactions product separations could be done by filtration [6]; while our reactions were carried out under homogeneous con-



Scheme 2. Proposed reaction mechanism for C–C bond formation reactions catalysed by magnesium carboxylates.

dition, hence the catalysts were to be separated by chemical means. However, the advantage of our system is the ease of preparation of the catalysts, starting from magnesium metal itself. To keep consistent morphology pre-screening is essential for the nano-particles or supported metal catalyst, which is not needed in the case of our catalysts and our catalysts are air-stable which do not degrade under ordinary condition.

In conclusion we have demonstrated a methodology of synthesis for magnesium carboxylate complexes from reactions of magnesium metal with methanol in the presence of aromatic carboxylic acids. Irrespective of parent carboxylic acids, the complexes are suitable catalyst for aldol condensation reactions. The C–C bond formation between aromatic aldehydes and acetone using magnesium benzoate complexes as catalysts is observed to give β -keto alcohols as the major product.

Acknowledgement

The authors thank Department of Science and Technology, New Delhi, India, for financial support.

References

- [1] J.W. Yun, T. Tanase, S.J. Lippard, *Inorg. Chem.* 35 (1996) 7590–7600.
- [2] C. Perrio-Huard, C. Aubert, M.-C. Lasne, *J. Chem. Soc. Perkin Trans. 1* (2000) 311–316.
- [3] N. Matsumura, T. Ohba, H. Inoue, *Bull. Chem. Soc. Japan* 55 (1982) 3949–3950.
- [4] G. Zhang, H. Hattori, T. Tanabe, *Appl. Catal.* 36 (1988) 189–197.
- [5] G. Zhang, H. Hattori, K. Tanabe, *Appl. Catal.* 40 (1988) 183–190.
- [6] H. Hattori, *Appl. Catal. A. Gen.* 222 (2001) 247–259.
- [7] A.L. Kantam, V. Balasubramaniam, K.B.S. Kumar, G.T. Venkanna, F. Figeras, *Adv. Synth. Catal.* 349 (2007) 1887–1890.
- [8] M. Dubey, B.G. Mishra, D. Sachdev, *Appl. Catal. A. Gen.* 338 (2008) 20–26.
- [9] K. Tanabe, G. Zhang, H. Hattori, *Appl. Catal.* 48 (1989) 63–69.
- [10] B.M. Choudary, M.L. Kantam, K.V.S. Ranganath, K. Mahendar, B. Sreedhar, *J. Am. Chem. Soc.* 126 (2004) 3396–3397.
- [11] M.L. Kantam, L. Chakrapani, T. Ramani, *Tet. Lett.* 48 (2007) 6121–6123.
- [12] M. Xu, M.J.L. Gines, A.-M. Hilmen, B.L. Stephens, E. Iglesia, *J. Catal.* 171 (1997) 130–147.
- [13] S.A. Ei-Molla, *Appl. Catal. A. Gen.* 298 (2006) 103–108.
- [14] A.K. Katz, J.P. Glusker, G.D. Markham, C.W. Bock, *J. Phys. Chem. B* 102 (1998) 6342–6350.
- [15] M.-L. Baily, C. Chizalli, G. Costentin, J.-M. Krafft, H. Lauron-Pernot, M. Che, *J. Catal.* 235 (2005) 413–422.
- [16] R.P. Davies, R.J. Less, P.D. Lickiss, A.J.P. White, *Dalton Trans.* (2007) 2528–2535.
- [17] Z. Hulvey, A.K. Cheetham, *Solid State Sci.* 9 (2007) 137–143.
- [18] M.T. Caudle, W.W. Brennessel, V.G. Young Jr, *Inorg. Chem.* 44 (2005) 3233–3240.
- [19] E.N. Coker, T.J. Boyle, M.A. Rodriguez, T.M. Alam, *Polyhedron* 23 (2004) 1739–1747.
- [20] A.N. Shnulin, G.N. Nadzhafov, I.R. Amiraslanov, B.T. Usabaliev, Kh. S. Mamedov, *Koord. Khim.* 7 (1981) 1409–1416.
- [21] T. Dudev, C. Lim, *Acc. Chem. Res.* 40 (2007) 85–93.
- [22] B.M. Choudary, L. Chakrapani, T. Ramani, K.V. Kumar, M.L. Kantam, *Tetrahedron* 62 (2006) 9571–9576.