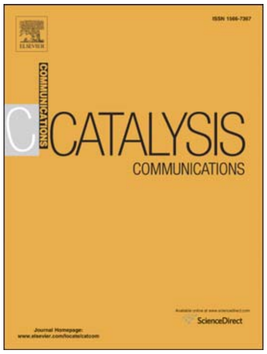


Highly efficient aerobic epoxidation of cyclic olefins in mild conditions by a novel binuclear manganese(II) complex containing *N*-(4-nitrophenyl)picolinamide ligand

Mojtaba Bagherzadeh, Alireza Ghanbarpour, Hamid Reza Khavasi

PII: S1566-7367(15)00082-5
DOI: doi: 10.1016/j.catcom.2015.02.023
Reference: CATCOM 4240

To appear in: *Catalysis Communications*

Received date: 17 December 2014
Revised date: 17 February 2015
Accepted date: 18 February 2015

Please cite this article as: Mojtaba Bagherzadeh, Alireza Ghanbarpour, Hamid Reza Khavasi, Highly efficient aerobic epoxidation of cyclic olefins in mild conditions by a novel binuclear manganese(II) complex containing *N*-(4-nitrophenyl)picolinamide ligand, *Catalysis Communications* (2015), doi: 10.1016/j.catcom.2015.02.023

Highly efficient aerobic epoxidation of cyclic olefins in mild conditions by a novel binuclear manganese(II) complex containing *N*-(4-nitrophenyl)picolinamide ligand

Mojtaba Bagherzadeh [a]*, Alireza Ghanbarpour, and Hamid Reza Khavasi [b]*

Abstract

A novel binuclear Mn(II) complex based on a *para*-nitro substituted amidic ligand (*N*-(4-nitrophenyl)picolinamide) has been synthesized and characterized by x-ray crystallography. This complex shows a high degree of conversion and epoxide selectivity in Mukaiyama aerobic epoxidation reactions of cyclic olefins in mild conditions.

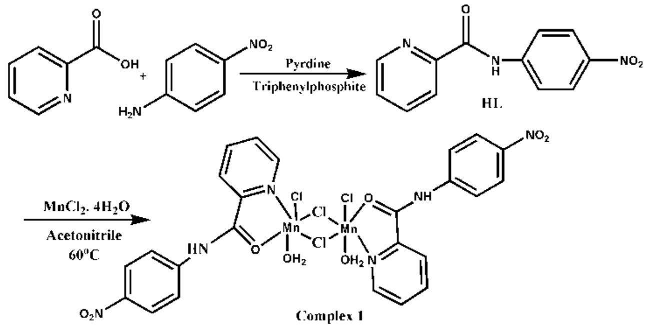
1-Introduction

Catalytic epoxidation reactions based on transition metal complexes have played an important role in organic synthesis and chemical industries since these reactions may provide epoxides as intermediates to generate useful chemicals [1,2]. Among catalytic epoxidation reactions, those which employ dioxygen as an oxidant have attracted great attention due to such advantages as having green nature and being inexpensive [3a]. However, using dioxygen, as an oxidant, usually has some disadvantages such as the low selectivity of products, the slow rate of reactions and production of by-products owing to overreacting [3]. Hence, to address these problems some co-reagents are used. Aldehydes are one of these co-reagent which may be utilized in the reactions referred to as Mukaiyama-Yamada epoxidation [4,5]. These reactions proceed through formation of acylperoxy radicals that preferentially react with double bonds of olefins to elicit epoxides. The role of metal catalyst, in these reactions, is not obvious completely; nevertheless, it has been proven that the metal catalyst can affect the initiation and the rate of reactions, as well as the selectivity of epoxide against allylic oxidation products [6,7]. Manganese complexes based on amidic ligands previously were used as efficient catalysts in these typical reactions [8-10]. Furthermore, over the past two decades, there has been such a great interest to study manganese redox enzymes, especially those which involve binuclear active sites [13]. Because of the paramount importance of manganese(II) complexes based on amidic ligands that can be used as model catalysts [13b] and the efficiency of them in Mukaiyama epoxidations, here, a new dimeric manganese(II) complex based on a *para*-nitro substituted amidic ligand has been synthesized and characterized by x-ray crystallography to evaluate its catalytic activity, in Mukaiyama epoxidation reactions, in comparison to its peers.

2-Experimental:

2.1. Catalyst preparation

As shown in scheme 1, complex (**1**) can easily be prepared from the direct reaction of *N*-(4-nitrophenyl)picolinamide molecule (HL) and $MnCl_2$. $4H_2O$ in acetonitrile in 60 ^oC in a convection tube (detailed procedure provided in supporting information file). HL can be synthesized by using the synthetic route we reported earlier and as it has been shown in Scheme 1 [14].



Scheme 1. Synthetic procedure of the amidic ligand and complex **1**.

2.2. Catalyst characterization

The suitable single crystal of complex 1 was also prepared through using the convection tube method (see supporting information file). The x-ray diffraction measurement was made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. Suitable single crystal was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data. The structural data and refinement for this compound is provided in Table S1.

3- Results and discussion

3.1. Crystal packing analysis

X-ray crystallographic data show that this compound crystalized in a triclinic system and the space group of $P\bar{1}$, Table S1**.** The crystal structure shows two manganese(II) centres with the distance of 3.642 Å which are connected to each other *via* two chloride bridged ions. Each Manganese centre has distorted octahedral geometry containing two oxygen atoms from two molecules of water, two bridged chloride ions, one chloride ion, one nitrogen and one oxygen atom from *N*-(4-nitrophenyl)picolinamide ligand, Figure 1. The bond distances and the angles of the coordination region has been provided in Table S2.The asymmetric unit of this compound involves one manganese atom, two chloride ions, a water molecule, a *N*-(4-nitrophenyl)picolinamide molecule, all of which are located in the coordination region of manganese, and an acetonitrile molecule which exists in its crystal packing (Z'=0.5), Figure 1.

Moreover, in the crystal packing, along *b*-axis, interactions such as $\pi_{ring\#1}\ldots\pi_{ring\#2}$ (with the centroid to centroid distance of 3.870), in cooperation with other weak interactions, generates a zigzag-like strand, each of which connects to its neighbour through bifurcated hydrogen bonds provided by the nitro substituent and a hydrogen atom of the phenyl ring of adjacent molecules (C2-H2…O2, C2-H2…O3, sym. code: -1+x, y, 1+z, Table S3). In addition, the water molecule coordinated to the metal centre can form hydrogen bond with acetonitrile molecule and traps it in the crystal packing of complex **1** (O4-H4B…N4, sym. code: 2-x, 2-y, -z, Table S3), Figure 2. There are also trifurcated hydrogen bonds (C12-H12….Cl1, N2-H2A…Cl1, C4-H4…Cl1, sym. code: 1-x, 3-y, 2-z, Table S3) giving a 2D-sheet in the represented direction, Figure 3.

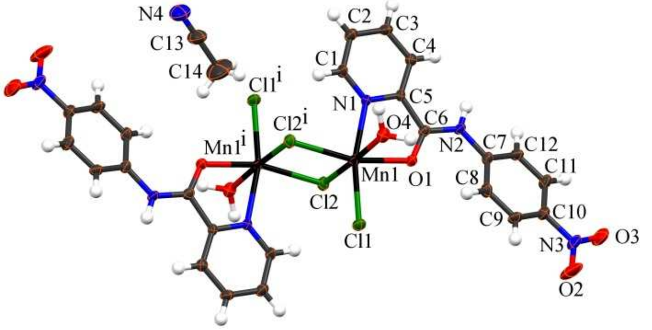


Figure 1. The ORTEP diagram of compound **1**. Ellipsoids at 50% probability level. Hydrogen atoms have been omitted for clarity. Symmetry code; *i*: 1+x,-1+y,z

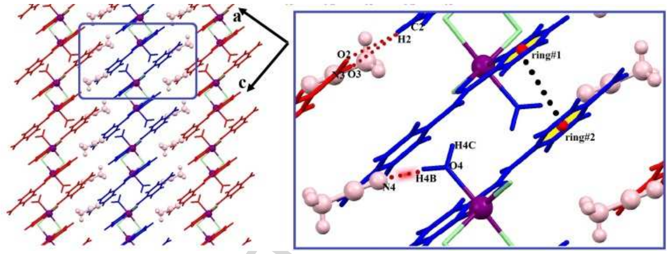


Figure 2. Representation of a zigzag-like strand which is made by $\pi_{ring\#1}\ldots\pi_{ring\#2}$ and other weak interactions**.** The Nitro substituents hydrogen bonds with phenyl ring of adjacent molecule to connect each strand to another one. The manganese (II) has been shown by purple, in Ball and Stick form. Acetonitrile solvent molecules have been illustrated by pink colour, in Ball and Stick representation.

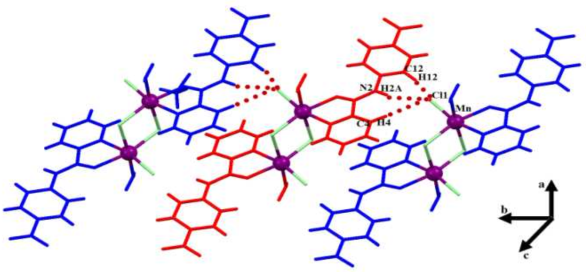


Figure 3. Trifurcated hydrogen bonds with three donors and one acceptor. The manganese (II) has been shown by purple, in ball and stick form.

3.2. Evaluation of catalyst

Based on our previous work in Mukaiyama epoxidation reactions [8] and noticing other reported results [9-12], this binuclear complex was designed and examined in aerobic epoxidation reactions with isobutyraldehyde as a co-reductant and different substrates. As illustrated in Table 1, complex 1 shows a significant conversion to product with the highest selectivity towards epoxide products. There is a general consensus that cyclohexene is the best substrate to evaluate the selectivity for epoxide versus allylic products since this substrate is very sensitive to the mechanism proceeding towards an allylic pathway, which can affect the ratio of epoxide to allylic products. Hence, this substrate was used for optimizing and studying the different conditions of catalytic reaction, Table 1. All of the reactions were monitored by gas chromatograph (Agilent Technologies 6890N Instrument, equipped with a capillary column 19019 J-413 HP-5, 5% phenyl methyl siloxane, capillary 60.0 m ×250μm ×1.00 μm, and a flame ionization detector).

Our results show that when reactions are catalysed by metal catalyst, the highest conversion and highest selectivity are achieved, Table 1 (entry1-4). In comparison to other similar amidic Mn(II) complexes, catalyst **1** is superior, according to its higher conversion and selectivity at room temperature. For example, in our previous work [8], when a binuclear Mn(II) complex based on *N*-((pyridin-2-yl)methyl)pyrazine-2-carboxamide ligand as a catalyst, isobutyraldehyde as a co-reagent, and DMF as a solvent, by the same stoichiometric amounts as this paper and in its optimum conditions , after 1 hour, the conversion of 24% was obtained in 60 °C, in the aerobic epoxidation of cyclohexene. Furthermore, in another similar work performed by Qi et al [10], when a mononuclear complex of Mn(II) based on N-(4-methyl phenyl) picolinamide ligand as a catalyst, isobutyraldehyde as a co-reagent, and 1,2-dichlroethane as a solvent were utilized, 59.6% of conversion and 92.2% of epoxide selectivity in room temperature were obtained in optimum conditions and the reaction completed after 13 hours. However, complex **1** is able to catalyse the aerobic epoxidation of cyclohexene, with isobutyraldehyde as a co-reagent, and 1,2-dichlroethane as a solvent, with conversion percentage of 80% in room temperature, and epoxide selectivity of >99%. Furthermore, the reaction approximately completes over 3 hours. Although the mechanism of metal complexes in Mukaiyama epoxidation reactions have not been understood thoroughly, by comparing the catalytic activity of catalyst **1** with other similar Mn(II) complexes based on amidic ligands, it is found that the efficiency of these reactions can vary with the electronic effect of ligands and coordination region of metal catalysts.

3.3. Optimization results of Catalytic system

To gain insight into the effect of other factors on the catalytic system, the effects of isobutyraldehyde concentration, catalyst amount, temperature effects, and radical scavenger were investigated, Table 1.

By doubling the amount of catalyst, the conversion increases from 80% to 95%, over 1 hour, entries1,4. Moreover, when the reaction is carried out without adding any catalyst, the conversion and selectivity decreases significantly, entry 8. Hence, it shows that the existence of metal catalyst may enhance conversion and epoxide selectivity. These results are consistent with the results of Wentzel and Mizuno et al about the role of metal catalysts in Mukaiyama epoxidation reactions [6]. Furthermore, this type of reaction, as reported earlier [6b,15], is sensitive to the amount of isobutyraldehyde. For instance, when isobutyraldehyde's amount is reduced to half of its initial concentration, the conversion reduces from 80% to 63% and if the reaction is performed without adding isobotyraldehyde, the conversion reduces significantly to 10% after 6 hours, entry 9. Furthermore, removing isobutyraldehyde leads to decreased selectivity for epoxide products. Moreover, using radical scavenger supports a fact that the reaction proceeds through radical mechanism since adding 2,6-di-tert-butyl-4-methylphenol, as a radical scavenger, the conversion decreases greatly, entry 12[b].

Table 1. Using **1** as a catalyst in the aerobic epoxidation of cyclohexene[a].

entry	***t(h)/ T(°C)***	**Catalyst (mmol)**	**Aldehyde (mmol)**	**Conversion (%)**	**Epoxide selectivity (%)**	TOF (min^{-1})
1	1/25	1.76×10^{-3}	1.76	80%	>99%	6.7
2	2/25	1.76×10^{-3}	1.76	96%	>99%	4.0
3	3/25	1.76×10^{-3}	1.76	>99%	>99%	2.8
4	1/25	3.52×10^{-3}	1.76	95%	>99%	3.9
5	1/0	1.76×10^{-3}	1.76	69%	>85%	5.7
6	1/35	1.76×10^{-3}	1.76	85%	>99%	7.1
7	1/25	1.76×10^{-3}	0.88	63%	95%	5.2
8	6/25	-	1.76	55%	75%	-
9	6/25	1.76×10^{-3}	-	10%	10%	0.1
10	6/25	6.40×10^{-3} ($MnCl_2$)	1.76	40%	70%	0.2
11	6/25	6.40×10^{-3} (free ligand)	1.76	58%	77%	0.8
12[b]	6/25	1.76×10^{-3}	1.76	1%	10%	0

a: Substrates (0.88 mmol), the catalyst (1.76×10^{-3} mmol), isobutyraldehyde (1.76 mmol), and pure O_2 (1 atm) in 2 mL of 1,2-dichlroethane as a solvent. Gas chromatography determination based on chlorobenzene as an internal standard. The main byproduct is 2-cyclohexen-1-one (from GC analysis). b: using 6.40×10^{-3} mmol of 2,6 -di-*tert*-butyl-4-methylphenol as a radical trapping compound.

In addition, decreasing the temperature from room to 0° C results in decreasing conversion (69%) and increasing temperature to 35° C leads to increasing conversion (85%). Therefore, it can be concluded that this catalytic system is sensitive towards reaction temperature and these results are in agreement with free radical chain mechanism [15b]. For further examining this catalytic system, the aerobic epoxidation four cyclic substrates have been studied, Table2. The results show a high amount of conversion to epoxide products; however, the more conversion percentage has been obtained for cyclohexene and its derivative (1-methyl-cyclohexne), which seems that catalyst **1** is more efficient for cyclohexenes in comparison to other cyclic olefins.

4-Conclusion

In conclusion, a dimeric manganese(II) complex based on N-(4-nitrophenyl) picolinamide ligand has been prepared and characterized by x-ray crystallography. The significant catalytic activities of this complex were obtained in aerobic Mukaiyama epoxidation of cyclic olefins under mild conditions. To the best of our knowledge, this amidic Mn(II) complex has a superior selectivity and conversion to epoxide products in comparison to other similar Mn(II) complexes based on amide ligands and especially can be a suitable candidate for aerobic epoxidation of cyclohexene in room temperature. These results may highlight the role of metal catalyst to elicit higher conversion in Mukaiyama epoxidation reactions.

Table 2. Conversion percentages of some cyclic olefins in Mukaiyama epoxidation reaction after 3 hours.

Substrate	**Conversion(%)**	**Epoxide selectivity(%)**
Cyclopentene	90%	>99%
1-methyl-cyclohexene	98%	>99%
Cycloheptene	84%	>99%
Cyclooctene	80%	>99%

The condition of reaction is: Substrate (0.88 mmol), catalyst (1.76×10^{-3} mmol), isobutyraldehyde (1.76 mmol), and pure O_2 (1 atm) in 2 mL of 1,2-dichlroethane as a solvent, in room temperature. Gas chromatography determination based on chlorobenzene as an internal standard. The main byproduct is 2-cyclohexen-1-one (from GC analysis)

Notes and references

[a] Department of Chemistry, Sharif University of Technology, Tehran 11155-3615, Iran, e-mail: bagherzadeh@sharif.edu

[b] Faculty of Chemistry, Shahid Beheshti University, G. C., Evin, Tehran 1983963113, Iran, e-mail: h-khavasi@sbu.ac.ir

Electronic Supplementary Information (ESI) available: Experimental details for synthesized compounds (CCDC No. 1008240), full crystallographic data, selected bond distances and bond angles and hydrogen bonding parameters.

References

[1] (a) L. Haughton and J. M. J Williams, *J. Chem. Soc., Perkin Trans.* 1, **1999**, 2645. b) K. A. Jorgenson, *Chem. Rev.* 2004, **104**, 1047.

[2] (a) M. Amini, M. M. Haghdoost, M Bagherzadeh, *Coord. Chem. Rev.*, 2014, **268**, 83. (b) M. Bagherzadeh, M. M. Haghdoost, A. Ghanbarpour, M. Amini, H. R. Khavasi, E. Payab, A. Ellern, L. K. Woo, *Inorg. Chim. Acta*, 2014, **411**, 61. (c) M. Amini, M. M. Haghdoost, M Bagherzadeh, *Coord. Chem. Rev.*, 2013, **257**, 1039. (d) M. Bagherzadeh, L. Tahsini, R. Latifi, *Catal. Commun*, 2008, **9**, 1600.

[3] (a) D. H. R. Barton, A. E Martell, D. T. Sawyer, The Activation of Dioxygen and Homogeneous Catalytic Oxidation; Plenum: New York, 1993. (b) J. Piera, J-E. Bäckvall, *Angew. Chem. Int. Ed.*, 2008, **47**, 3506. (c) T. Punniyamurthy, S. Vellusamy, and J. Iqbal, Chem. Rev., 2005, **105**, 2329.

[4] (a) T. Yamada and T. Mukaiyama, *Chem. Lett.*, 1989, **18**, 519. (b) T. Yamada, K. Imagawa, and T. Mukaiyama, *Chem. Lett.* 1992, **21**, 2109.

[5] K. R. Rodgers, I. M. Arafa, and H. M. Goff, *J. Chem. Soc., Chem. Commun.*, 1990, **19**, 1323.

[6] (a) B. B. Wentzel, P. L. Alsters, M. C. Feiters, and R. J. M. Nolte, *J. Org. Chem.*, 2004, **69**, 3453. (b) N. Mizuno, H. Weiner, R. G. Finke, *J. Mol. Catal. A: Chem.* 1996, **114**, 15. (C) B. B Wentzel, P.A. Gosling, M. C. Fieters, R. J. M Nolte, *J. Chem. Soc., Dalton Trans*, 1998, **13**, 2241.

[7] W. Nam, H. J. Kim, S. H. Kim, R. Y. N. Ho, and J. S. Valentine, *Inorg. Chem.*, 1996, **35**, 1045.

[8] H. R. Khavasi, K. Sasan, M. Pirouzmand, and S. N. Ebrahimi, *Inorg. Chem.* 2009, **48**, 5593.

[9] C-M. Che and W-K. Cheng, *J. Chem. Soc., Chem. Commun.*, **1986**,1443.

[10] J.-Y. Qi, Y.M Li, Z. Y Zhou, C. M. Che, C. H. Yeung, A. S. C. Chan, *Adv. Synth. Catal.* 2005, **347**, 45.

[11] Z. Li, C. Liu, R. Tang, and G. Liu, *RSC. Adv.*, 2013, **3**, **9745.**

[12] J. Y. Qi, L. Q. Qiu, K. H. Lam, C. W. Yip, Z. Y. Zhou, A. S. C. Chan, *Chem. Commun*, **2003**, 1058.

[13] (a) A. Willing, H. Follmann, G. Auling, *Eur. J. Biochem.*, 1988, **178**, 603. (b) K. Wieghardt, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 1153.

[14] H. R. Khavasi, A. Ghanbarpour, A. A. Tehrani, *CrystEngComm.* 2014, **16**, 749.

[15] (a) T.V. Filippova, E.A. Blyumberg, *Russ.* ***Chem. Rev***, 1982, **51**, 582. (b) C. L. Hill, *Nature*, 1999, **401**, 436.

Highlights

- Structural study of a novel binuclear Mn(II) complex
- Evaluation of catalyst in Mukaiyama Epoxidation reaction
- Eliciting the higher efficiency in aerobic epoxidation of cyclic olefins