Commun. Comput. Chem. Vol.**3**, No.**2**, pp.35-43
doi: 10.4208/cicc.2015.v3.n2.1 September 2015

## COMMUNICATION

# Theoretical Study on Sulfoxidation Reactivity by a Nickel Acylperoxo Complex

Huiling Song[†,#], Xiaoqian Zhang[‡], Qiao Qing-An[†,*] and Yong Wang[#,§,]

[†] *School of Chemistry and Materials Science, Ludong University, Yantai 264025, China*

[‡] *College of Physics and Electronic Engineer, Henan Normal University, Xinxiang 453007, China*

[#] *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China*

[§] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, China*

Received 20 May 2015; Accepted (in revised version) 13 July 2015

**Abstract:** The mechanism of the biomimetic nonheme complexes has been experimentally and theoretically studied in recent years, owing to their capability to activate various substrates. According to the previous studies, the mechanisms were different in the presence/absence of acid. In this paper, we used density functional theoretical (DFT) methods to study the mechanism of the sulfoxidation of sulfide by a nickel acylperoxo complex [Ni-($Tp^{CF3Me}$)($\kappa^2$-mCPBA)] in the presence of the *m*-chloroperbenzoic acid(mCPBA). Both the concerted and the stepwise radical mechanisms were proposed and it was demonstrated that the former is preferred.

**AMS subject classifications:** 65D18, 74M40, 78M50

**Keywords:** nickel acylperoxo complex, sulfoxidation, concerted mechanism

## Introduction

In the past few years, a large number of biomimetic nonheme complexes have been designed and developed to catalyze the hydroxylation, epoxidation, or cis-dihydroxylation

* Corresponding author. *Email address*: wangyong@licp.cas.cn (Y. Wang)
qiaoqa@ldu.edu.cn (Q. –A. Qiao)

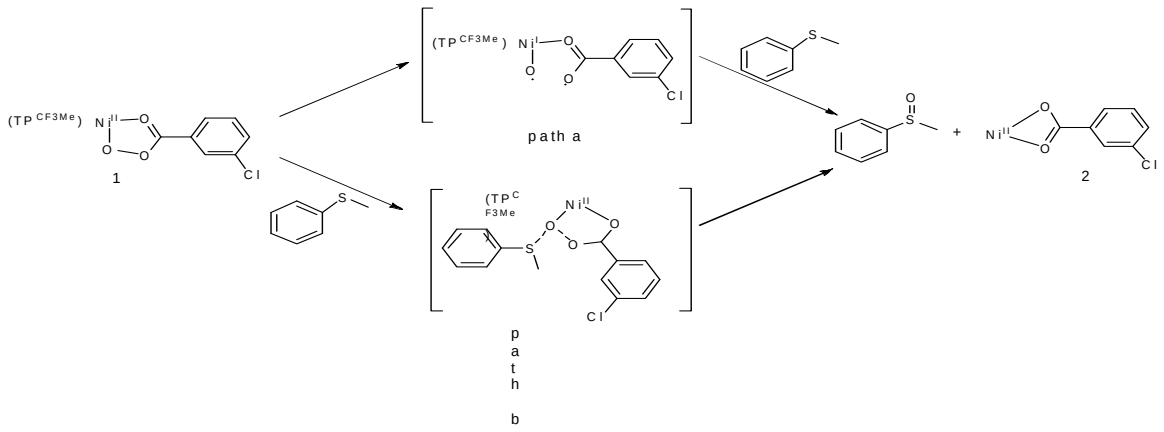
of hydrocarbon substrates with high stereoselectivity [1-3]. Despite intensive research efforts, the catalysis mechanism was still a formidable challenge to chemists, especially for the genuine oxidant and intermediate involved. Thus, experimental and theoretical studies have been performed to investigate the mechanism, which may lead to new insight in biocatalysis as well as enlighten new approaches for industrial catalysis.

According to the previous studies, it was found that the mechanisms were different with and without acid. In 2001, Que et al. proposed a general mechanism for alkane oxidation by $Fe^{II}$(TPA) (TPA=tris(3,5-dimethyl-4-methoxypyridyl-2-methyl)amine) family of catalysis in combination with $H_2O_2$, in which both $Fe^{III}$-OOH and $Fe^{V}$(O)OH oxidants could play a vital role in alkane hydroxylation [4]. In 2006, Que et al. characterized a family of nonheme iron catalysts and performed olefin epoxidation, cis-dihydroxylation using $H_2O_2$ as the oxidant. The resultant intermediate was observed as the ferric hydroperoxo complex $Fe^{III}$-OOH, whose spin state was modulated by the electronic and steric properties of the ligand environment. In $Fe^{II}$(TPA)/$H_2O_2$/$H_2O$ system, the intermediate is $Fe^{III}$-OOH, which decays via water-assisted heterolytic O-O bond cleavage to form a real oxidant $Fe^{V}$(O)OH [5, 6]. The kinetic evidence for such pathway and the mass spectral evidence of the oxidant has been reported [7,8]. Overall, the available data reveal a surprising complex reaction landscape that the transformation is carried out by the common $Fe^{V}$(O)OH oxidant.

The addition of acetic acid could alter the mechanism and improve both catalytic activity and selectivity [6, 9-11]. In the $Fe^{II}$(TPA)/$H_2O_2$/AcOH system, Que et al. [12] have observed the intermediate and it was proposed that the oxidant was the [(TPA)$Fe^{V}$(O)(OC(O)$CH_3$)], Talsi et al. performed EPR spin trapping and found that g=2.7 [13]. The further support has also been built on the basis of DFT calculations. Gopalan et al. explored two possible high-valent species generated from the cleavage of O-O bond of $Fe^{III}$-OOH species, which revealed that the species underwent heterolytic cleavage to form a transient $Fe^{V}$=O oxidant, then it underwent an electrophilic attack and eventually led to the ortho-hydroxylated product [14]. Wang et al. also performed the calculations, and the results showed that the oxidant was an oxoiron (V) species [(TPA)$Fe^{V}$(O)(OC(O)$CH_3$)] which was isomerized by [(TPA)$Fe^{IV}$(O)(OC(O)$CH_3$) radical] [15]. Que et al. observed the change in olefin oxidation products when the acetic acid replaced the water and they proposed the modification of the water-assisted mechanism to a carboxylic-acid-assisted version [16]. In the $Fe^{II}$(S,S)-PDP/$H_2O_2$/AcOH system [17], the catalyst was the cyclic ferric peracetate complex and it could convert to a transient oxoiron (IV)-ACO species that performed alkane hydroxylation. Elena and co-workers observed the unusual g=2.7 EPR signal in the presence of carboxylic acid and postulated that this chromophore was an acylperoxoiron(III) intermediate and the oxidant might be unobserved higher-valent oxidant [18].

Nickel has recently emerged as an attractive transition metal for the development of catalysts. It is reported that nickel acylperoxo complexes have strong oxidative activity. Recently Hikichi Shiro and co-workers had characterized the nickel(II)-acylperoxo complex which showed electrophilic oxygenation toward sulfides and olefins with the addition of mCPBA [19]. It could catalyze a variety of substrates via oxygenation transformations, such as selective partial of alkane, olefin epoxidations and sulfoxidatons. Besides, the electronic and steric hindrance properties of the supporting ligands affect the catalytic activity as well as the alcohol/ketone(A/K) selectivity [19-22]. For nickel acylperoxide, it is generally believed that the Ni -O. free radical is formed through O - O homolysis, followed by the attack from the radical to the substrate [22,23]. However, there is no exact theoretical or experimental evidence for the existence of the radical. To shed light on the mechanism of the nickel(II)-acylperoxo, we performed the theoretical calculations. In this paper, ($Tp^{CF3Me}$) was employed as the Ni-supporting ligand because the proximal trifluoromethyl groups exhibit an electron-withdrawing nature, high oxidation resistance, and moderate steric hindrance. The versatility of $Tp^{CF3Me}$ for the stabilization of metal−dioxygen species was revealed by the Cu complex [23]. Therefore, we choose [Ni-($Tp^{CF3Me}$)] as the catalyst.

According to the previous studies, herein we proposed two possible mechanisms as shown in **Scheme 1**. Firstly, [Ni-($Tp^{CF3Me}$)(κ2-mCPBA)] is formed as precursor. Then, there are two possible pathways. Path a, O-O bond homolysis may occur to give the [$TP^{CF3Me}$ NiI (O)] and $ArCO_2$ moieties. The former is the active oxidant and can react with sulfide directly to generate sulfoxide and [Ni-($Tp^{CF3Me}$)(κ2-mCBA)]. Path b, the precursor reacts with substrate via a concerted mechanism through concomitant O-O rupture and oxygen atom transfer.




**Scheme 1** Two possible mechanisms proposed for the sulf-oxidation.

## Methods

The coordinates of [Ni-($Tp^{CF3Me}$)($\kappa^2$-mCPBA)] was obtained from Cambridge Crystallographic Data Centre. DFT calculations were performed with the Gaussian 09 suite of quantum chemical packages using the B3LYP/LACVP* computational level under the temperature of 233.15K in toluene solvent. All optimizations and single-point calculations were performed with solvation using the self-consistent reaction field (SCRF) calculations in the polarizable continuum model (PCM). Experience has shown that the obtained structures using such methods were adequate for the calculations [19]. The transition states were ascertained by vibrational frequency analysis to possess a single mode along the reaction path with only one imaginary frequency. The spin populations reported were derived from the Mulliken population analysis.

## Results and discussion

In this paper, we studied the singlet and triplet states of compound **1**. The triplet state is found to be the ground state, with the singlet and quintet 18.0 and 61.7 kcal/mol higher in energy respectively (Table S1 in SI).

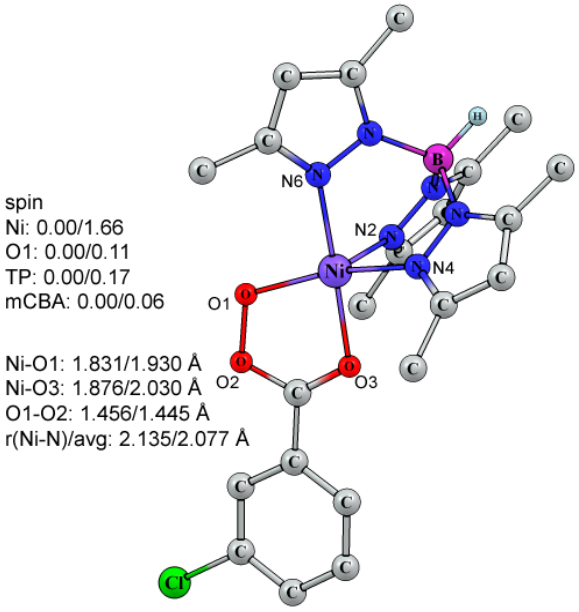



**Figure 1:** UB3LYP/LACVP* optimized geometries and spin densities of complex **1** with selected structural parameters. Hydrogen and fluorine atoms are omitted for clarity.

As shown in Table 1, the difference of bond length between experiment and calculation is less than 0.033 Å(Ni-N2), which indicates that our calculations are reasonable. The compound **1** is a penta-coordinated compound with three N atoms from pyrazole ring and two O atoms from mCPBA. The compound **1** is a neutral complex in which the oxidation state of Ni is +2. The optimized structure parameters are consistent with previous experimental findings [19]. As **Figure 1** revealed, Ni of $^{3}$**1** has large spin density whereas mCBA has small one.

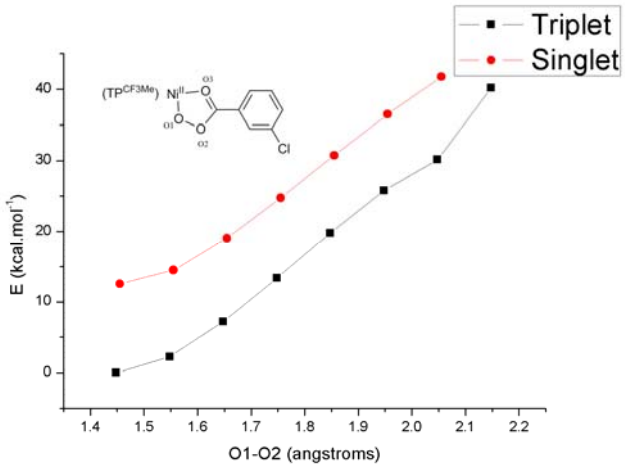



**Figure 2**: UB3LYP/LACVP* computed relaxed potential-energy scan for the O1-O2 cleavage of singlet and triplet of complex **1**.

To better elucidate the electronic structures of $^{3}$**1**, the spin natural orbitals (SNOS) have been shown in Figure S2. According the previous studies, we proposed two proposals on the reaction paths, one is radical stepwise manner, the other is concerted.

Path a. First, we performed the relaxed scan of O1-O2 cleavage as shown in **Figure 2**. The barrier of O1-O2 cleavage is computed more than 35kcal/mol for both singlet and triplet spin state. Considering the large barrier height is encountered in path a, we can definitely ignore the possibility of path a.

**Table 1** The difference between experiment and calculation on the bond distance.

| Bond distances/Å | Ni-N2 | Ni-N4 | Ni-N6 | r(Ni-N)/avg | Ni-O1 | O1-O2 | Ni-O3 |
|---|---|---|---|---|---|---|---|
| experiment | 2.037 | 2.041 | 2.058 | 2.045 | 1.914 | 1.445 | 2.040 |
| calculation | 2.070 | 2.070 | 2.089 | 2.077 | 1.930 | 1.445 | 2.030 |
| d/Å | 0.033 | 0.029 | 0.031 | 0.032 | 0.016 | 0.000 | -0.010 |

Path b: As previously proposed and shown in **Scheme 2,** we considere that the mechanism is concerted. O1-O2 bond cleavage occurs along with the sulphur atom close to O1 and the computed profile is shown in **Figure 3**.

As shown in **Figure 3**, the barrier height for O1-O2 cleavage is computed to be 12.6 and 16.5 kcal/mol for the triplet and singlet spin states. **Figure 3** also depicts the structural parameters. As shown in **Figure 3,** as the sulphur atom attacks O1, S-O1 is decreased from 2.215 Å of the transition state to the 1.567 Å of the product, O1-O2 bond is increased from 1.445 Å to 1.767 Å simultaneously. Ni-O1 bond is also increased from 1.942 Å to 1.987 Å. We also analyze the vibrational frequency of the transition and find both the triplet and the singlet states possess a single mode with only one imaginary frequency.

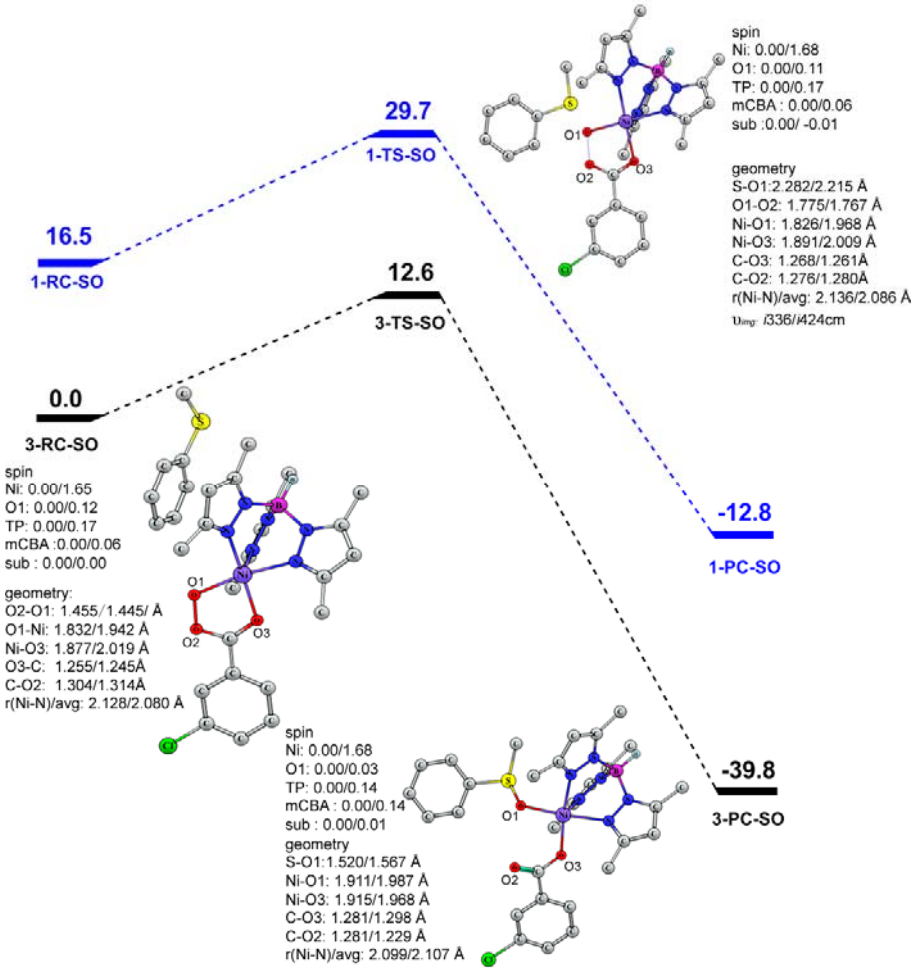
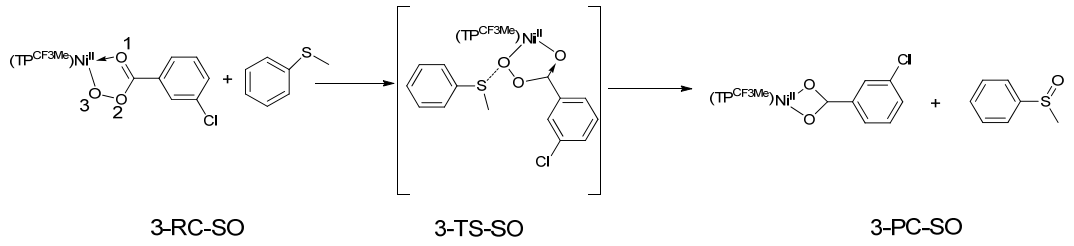



**Figure 3**: Energy profiles (kcal/mol) and geometries and spin densities of the transition state. Hydrogen and fluorine atoms are omitted for clarity.




**Scheme 2** path b: the concerted mechanism.

# Conclusions

DFT calculations have been performed to explore the mechanism of sulfoxidation of thioanisole with **1**. We have explored various possible reaction pathways in the course of sulfoxidation. According our calculations, path a is impossible due to the large energy barrier height, and the sulfoxidation is performed by the attack of **1** to the sulfide directly. The results indicate that the radical-mediated manner proposed preciously is impossible. This study can provide guidance to the design of the nonheme biomemic catalysis.

# Acknowledgments

W.Y. gratefully acknowledges research support from the National Natural Science Foundation of China (grants 21003116 and 21173211). This work was financially supported by Shandong Provincial Natural Science Foundation of China (Grant ZR2014BM037).

**Associated content**

Supporting information: Five figures and five tables are presented to describe the mechanistic details. Cartesian coordinates of all involved complexes are also presents.

**REFERENCES**

[1] V. C. Ezeh, T. C. Harrop, A Sensitive and Selective Fluorescence Sensor for the Detection of Arsenic(III) in Organic Media. Inorg. Chem. 51 (2012), 1213-1215.

[2] W. Nam, I. Kim, Y. Kim, C. Kim, Biomimetic alkane hydroxylation by cobalt(III) porphyrin complex and m-chloroperbenzoic acid. Chem. Commun. 14 (2001), 1262-1263.

[3] K. Chen, L. Que, Stereospecific alkane hydroxylation by non-heme iron catalysts Mechanistic evidence for an Fe-V = O active species. J. Am. Chem. Soc. 123 (2001), 6327-6337.

[4] V. C. Ezeh, T. C. Harrop, Synthesis and Properties of Arsenic(III)-Reactive Coumarin-Appended Benzothiazolines A New Approach for Inorganic Arsenic Detection. Inorg. Chem. 52 (2013), 2323-2334.

[5] W. N. Oloo, A. J. Fielding, L. Que, Rate-determining water-assisted O-O bond cleavage of an Fe(III)-OOH intermediate in a bio-inspired nonheme iron-catalyzed oxidation. J. Am. Chem. Soc. 135 (2013), 6438-6441.

[6] R. Mas-Balleste, M. Fujita, C. Hemmila, L. Que, Bio-inspired iron-catalyzed olefin oxidation. Additive effects on the cis-diol/epoxide ratio. J. Mol. Catal. A: Chem. 251 (2006), 49-53.

[7] I. Prat, J. S. Mathieson, M. Guell, X. Ribas, J. M. Luis, L. Cronin, M. Costas, Observation of Fe(V)=O using variable-temperature mass spectrometry and its enzyme-like C-H and C=C oxidation reactions. Nat. Chem. 3 (2011), 788-793.

[8] O. Y. Lyakin, I. Prat, K. P. Bryliakov, M. Costas, E. P. Talsi, O. Y. Lyakin, EPR detection of Fe(V)=O active species in nonheme iron-catalyzed oxidations. Catal. Commun. 29 (2012), 105-108.

[9] M. C. White, A. G. Doyle, E. N. Jacobsen, A synthetically useful, self-assembling MMO mimic system for catalytic alkene epoxidation with aqueous H2O2. J. Am. Chem. Soc. 123 (2001), 7194-7195.

[10] R. Mas-Balleste, L. Que, Iron-catalyzed olefin epoxidation in the presence of acetic acid Insights into the nature of the metal-based oxidant. J. Am. Chem. Soc. 129 (2007), 15964-15972.

[11] E. A. Duban, K. P. Bryliakov, E. P. Talsi, The active intermediates of non-heme-iron-based systems for catalytic alkene epoxidation with H2O2/CH3COOH. Eur. J. Inorg. Chem. 6 (2007), 852-857.

[12] A. Collado, A. Gomez-Suarez, Y. Oonishi, A. M. Slawin, S. P. Nolan, Synthesis, characterisation, and oxygen atom transfer reactions involving the first gold(I)-alkylperoxo complexes. Chem. Commun. 49 (2013), 10745-10747.

[13] O. Y. Lyakin, K. P. Bryliakov, G. J. Britovsek, E. P. Talsi, EPR Spectroscopic Trapping of the Active Species of Nonheme Iron-Catalyzed Oxidation. J. Am. Chem. Soc. 131 (2009), 10798-10799.

[14] A. Ansari, A. Kaushik, G. Rajaraman, Mechanistic insights on the ortho-hydroxylation of aromatic compounds by non-heme iron complex a computational case study on the comparative oxidative ability of ferric-hydroperoxo and high-valent Fe(IV) horizontal lineO and Fe(V) horizontal lineO intermediates. J. Am. Chem. Soc. 135 (2013), 4235-4249.

[15] W. N. Oloo, K.K. Meier, Y. Wang, S. Shaik, E. Münck, L. Que, Identification of a low-spin acylperoxoiron(III) intermediate in bio-inspired non-heme iron-catalysed oxidations. Nat. Commun. 5 (2014), 155-164.

[16] J. Agarwal, B. C. Sanders, E. Fujita, H. F. Schaefer, T. C. Harrop, J. T. Muckerman, Exploring the intermediates of photochemical CO2 reduction reaction of Re(dmb)(CO)(3) COOH with CO2. Chem. Commun. 48 (2012), 6797-6799.

[17] Y. Wang, D. Janardanan, D. Usharani, K. L. Han, Nonheme Iron Oxidant Formed in the Presence of $H_2O_2$ and Acetic Acid Is the Cyclic Ferric Peracetate Complex, Not a Perferryloxo Complex. ACS Catalysis. 3 (2013), 1334-1341.

[18] D. Shen, C. Miao, S. Wang, S. Wei, Efficient Benzylic and Aliphatic C-H Oxidation with Selectivity for Methylenic Sites Catalyzed by a Bioinspired Manganese Complex. Org. Lett. 16 (2014), 1108-1111.

[19] J. Nakazawa, S. Terada, M. Yamada, S. Hikichi, Structural characterization and oxidation reactivity of a nickel(II) acylperoxo complex. J. Am. Chem. Soc. 135 (2013), 6010-6013.

[20] M. Sankaralingam, P. Vadivelu, E. Suresh, M. Palaniandavar, Mixed ligand nickel(II) complexes as catalysts for alkane hydroxylation using m-chloroperbenzoic acid as oxidant. Inorg. Chim. Acta. 407 (2013), 98-107.

[21] S. Hikichi, K. Hanaue, T. Fujimura, J. Nakazawa, Y, Ohzu, C. Kobayashi, M. Akita, Characterization of nickel(II)-acylperoxo species relevant to catalytic alkane hydroxylation by nickel complex with mCPBA. Dalton Trans. 42 (2013), 3346-3356.

[22] M. Balamurugan, R. Mayilmurugan, E. Suresh, M. Palaniandavar, Nickel(II) complexes of tripodal 4N ligands as catalysts for alkane oxidation using m-CPBA as oxidant ligand stereoelectronic effects on catalysis. Dalton Trans. 40 (2011), 9413-9424.

[23] Z. B. Hu, G. N. George, S. M. Gorun, Fluorine encapsulation and stabilization of biologically relevant low-valence copper-oxo cores. Inorg. Chem. 40 (2001), 4812-4813.