Novel Cage-Like Hexanuclear Nickel(II) Silsesquioxane. Synthesis, Structure, and Catalytic Activity in Oxidations with Peroxides

Alexey N. Bilyachenko 1,2,*, Alexey I. Yalymov 1, Lidia S. Shul’pina 1, Dalmo Mandelli 3, Alexander A. Korlyukov 1,4, Anna V. Vologzhanina 1, Marina A. Es’kova 1, Elena S. Shubina 1, Mikhail M. Levitsky 1 and Georgiy B. Shul’pin 5,6,*

1 Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str. 28, 119991 Moscow, Russia; alexyalymov@gmail.com (A.I.Y.); shulpina@ineos.ac.ru (L.S.S.); alex@xrlab.ineos.ac.ru (A.A.K.); vologzhanina@mail.ru (A.V.V.); marinaeskovskaya@gmail.com (M.A.E.); shu@ineos.ac.ru (E.S.S.); levitsk@ineos.ac.ru (M.M.L.)
2 Inorganic Chemistry Department, People’s Friendship University of Russia, Miklukho-Maklay Str. 6, 117198 Moscow, Russia
3 Center of Natural and Human Sciences, Federal University of ABC (UFABC), Santa Adélia Street, 166, Bangu, Santo André, SP 09210-170, Brazil; dalmo.mandelli@ufabc.edu.br
4 Chemistry Department, Russian National Research Medical University, Ostrovitianov str. 1, 117997 Moscow, Russia
5 Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina, dom 4, 119991 Moscow, Russia
6 Chair of Chemistry and Physics, Plekhanov Russian University of Economics, Stremyannyi pereulok, dom 36, 117997 Moscow, Russia
* Correspondence: bilyachenko@ineos.ac.ru (A.N.B.); shulpin@chph.ras.ru (G.B.S.);
Tel.: +7-499-135-9369 (A.N.B.); +7-495-939-7317 (G.B.S.)

Academic Editor: Maxim L. Kuznetsov
Received: 12 April 2016; Accepted: 13 May 2016; Published: 19 May 2016

Abstract: New hexanuclear nickel(II) silsesquioxane [(PhSiO1.5)12(NiO)6(NaCl)] (1) was synthesized as its dioxane-benzonitrile-water complex (PhSiO1.5)12(NiO)6(NaCl)(C4H8O2)13(PhCN)2(H2O)2 and studied by X-ray and topological analysis. The compound exhibits cylinder-like type of molecular architecture and represents very rare case of polyhedral complexation of metallasilsesquioxane with benzonitrile. Complex 1 exhibited catalytic activity in activation of such small molecules as light alkanes and alcohols. Namely, oxidation of alcohols with tert-butylhydroperoxide and alkanes with meta-chloroperoxybenzoic acid. The oxidation of methycyclohexane gave rise to the isomeric ketones and unusual distribution of alcohol isomers.

Keywords: metal silsesquioxane; X-ray analysis; topological analysis; oxidation; alkanes; alcohols; meta-chloroperoxybenzoic acid (MCPBA)

1. Introduction

Cage-like metallasilsesquioxanes (CLMSs) [1–13], being a family of polyhedra with inorganic (metal silicate-like) cores and organic environments, have been thoroughly investigated in the line of their potential application in catalysis [14–17]. Nevertheless, their capacities as catalysts of oxidation processes remain in the shadow until recent past. Then, some of us reported the first examples of the oxidation reactions catalyzed by copper(II) silsesquioxanes, possessing different types of cage geometry, namely cooling tower [18,19], globule [19,20], sandwich [20], and cylinder [21].

To use the advantage of good solubility of cage metallasilsesquioxanes in organic solvents and the ability of bringing unusual effects in the catalytic act due to specific structures of catalytic centers [19]...
we decided to study some other (not copper-containing) types of CLMSs. Here we present preliminary results on first examination of new Ni(II)-CLMS under oxidation conditions.

2. Results and Discussion

2.1. Synthesis

Recently, some of us reported on ability of 1,4-dioxane molecules to serve as bridging linkers, combining individual CLMSs into an entire supramolecular system [20], and we were interested in the synthesis of new dioxane-CLMS complexes. Performing the synthesis of Ni-phenylsilsesquioxane [starting from PhSi(OEt)₃] in dioxane-containing media allowed us to isolate (in 20% yield) a new cage-like hexanuclear product [(PhSiO₁.₅)₁₂(NiO)₆(NaCl)] (1) in the form of its adduct with dioxane/benzonitrile/water solvating ligands (PhSiO₁.₅)₁₂(NiO)₆(NaCl)(C₄H₈O₂)₁₃(PhCN)₁₂(H₂O)₂ (Scheme 1).

\[
\text{PhSi(OEt)}₃ + 2\text{H}_2\text{O}, \text{NaOH (MeOH)} \xrightarrow{\frac{1}{2} \text{Ni(NH}_3)₆\text{Cl}_2 \text{ (dioxane, PhCN)}} \text{[(PhSiO}_1.₅)₁₂\text{(NiO)}₆\text{(NaCl)}]}
\]

Scheme 1. Synthesis of compound 1.

2.2. Structure

The age skeleton of the product belongs to a CLMS of the cylinder type [9], characterized by the presence of three layers: two 12-membered siloxane cycles mutually connected through a metal-oxide (Ni₆O₆) cycle (Figure 1; see Supplementary Materials for more details).

![Figure 1](image-url) Molecular structure of compound 1 (A—side view, B—top view). Solvating ligands and counter ion Na⁺ are omitted for clarity.

The inner void of the cylinder moiety contains a chloride anion which occupies the crystallographic center of inversion. Each Ni(II) ion of 1 adopts distorted octahedral coordination. The axial positions of the octahedron are occupied by a Cl⁻ anion and oxygen or nitrogen atoms of coordinated dioxane and benzonitrile molecules, respectively. Four nickel ions of 1 are coordinated by dioxane molecules, while the remaining two ions are bonded to benzonitrile molecules (Figure 2). Possibly, the donor ability of solvent molecules can govern the strength of Ni···Cl coordination bond and distortion of cylindric shape as consequence. Indeed, Ni···Cl distances are noticeably different [2.7231(7), 2.8269(8) and 2.9474 Å]. It is noteworthy, that shortest Ni···Cl distances correspond to nickel atoms coordinated by dioxane molecules.
This is just the second evidence that benzonitrile ligands could participate in aggregation of a CLMS structure. The first observation of such unusual coordination was presented by some of us [21] for the copper-containing CLMS.

2.3. Topological Analysis and Supramolecular Assembly

Following the procedure of a metal cluster notation [22] implemented into the ToposPro package (the Samara Center for Theoretical Materials Science, Samara, Russia) [23] we obtained that nickel atoms in compound 1 form in terms of the NDk-m notation the discrete 5M6-1clusters, where 5 is the coordination number of topologically non-equivalent nodes, M denotes a discrete cluster, 6 is the number of metal atoms in the cluster, and 1 is a classification number to distinguish topologically-distinct clusters with equal NDk parameters. A database of topological representations of polynuclear nickel compounds [24] contains representatives of the nickel clusters with the 5M6-1 topology, and μ6-coordinated Hal− and S2− anions; recently, some of us have synthesized a nickel-silsesquioxane encapsulating the O2− anion [13]. Nevertheless, to our knowledge, complex 1 is only the sixth known representative of Ni6 clusters with the 5M6-1 topology.

An additional attractive feature of synthesized complex is a formation of supramolecular structure where cage components are assembled into infinite chains (Figure 3) via H-bonds between water molecules bonded to sodium anions and oxygen atoms of siloxane cycles. The r(O...O) and ∠OHO are equal to 3.364(6)–3.488(6) Å and 135.7°–149.0°. The connection between ions is additionally supported
by C-H···O interactions between 1,4-dioxane and silsesquioxane as short as 3.62(2) and 3.91(2) Å for r(O···C). As a consequence, cylinder cage fragments and complex cations Na(H2O)2(O2C4H8)2 share the same pseudo two-fold axis parallel to the [100]-crystallographic direction. The chains are packed as the hexagonal rod packing, with the distances between two-fold axes of 16.1 and 16.3 Å and non-parallel disposition of Ni6 metal rings. Only weak C-H···O and C-H···π bonding between neighboring chains, or chains and solvent molecules, were found. Worth noting is that the shortest distance between two oxygen atoms of 1,4-dioxanes connected with Ni is equal to 8.6 Å, which is only slightly longer than the distance between nitrogen atoms of 4,4′-bipyridine, at 7.1 Å. In principle, this means that bipyridine and its analogues can be used to obtain coordination polymers connected by linkers through d-metals even for bulky phenylsilsesquioxanes. This opportunity will be a subject of our further investigations.
2.4. Oxidations Catalyzed by Compound 1

Nickel complexes are known to catalyze certain oxidation reactions of hydrocarbons [25–37] and alcohols [38–44] by peroxides. We have tested the catalytic effect of compound 1 in oxidations with various oxidants. It turned out that 1 does not catalyze the oxidation of 1-phenylethanol or alkanes with hydrogen peroxide in acetonitrile solution. In contrast to H$_2$O$_2$, tert-butyl hydroperoxide oxidizes 1-phenylethanol at 70 °C to afford acetophenone in 90% yield (initial reaction rate $W_0 = 7 \times 10^{-6}$ M s$^{-1}$; initial TOF = 50 h$^{-1}$) after 24 h. The kinetic curves of acetophenone accumulation shown in Figure 4 indicate the pronounced catalytic effect of compound 1.

![Figure 4](image)

**Figure 4.** Formation of acetophenone with time in the 1-phenylethanol (0.33 M) oxidation with tert-butyl hydroperoxide (TBHP; 70%, aqueous, 1.65 M) in the absence and in the presence of compound 1 (5 × 10$^{-4}$ M), as well as in the presence of Ni(NO$_3$)$_2$. Solvent was acetonitrile (total volume of the reaction solution was 5 mL); temperature was 70 °C.

As can be expected, alkanes are less reactive in comparison with alcohols and only meta-choroperoxybenzoic acid (m-CPBA) turned out to be a good oxidant. Certain complexes of transition metals have been previously reported to oxidize alkanes with m-CPBA [27–29,32–34,36,45–47]. Complex 1 exhibited activity in the oxidation of cyclohexane with m-CPBA (Table 1). It can be seen that at 20 °C the reaction deceased after 15 min. The ketone/alcohol ratio is not changed in the chromatograms made before and after reduction of samples with triphenylphosphine. This indicates that cyclohexyl hydroperoxide is not formed in the course of the oxidation (for this simple method, see [48–51]). The yield of oxygenates was 24% and TON = 64, TOF = 256 h$^{-1}$.

The oxidation of n-octane (0.12 M) with m-CPBA (0.13 M) in the presence of compound 1 (5 × 10$^{-4}$ M) and co-catalyst HNO$_3$ (0.05 M) at 60 °C during 3 h gave rise to the formation of a mixture of 2-, 3-, and 4-octanones (0.009, 0.009, and 0.008 M, respectively; yield 22%; TON = 52, TOF = 208 h$^{-1}$). The oxidation of methylcyclohexane under similar conditions gave predominantly isomeric ketones (products P2–P4; M) and tert-alcohol P5 (M; Figures 5 and 6). Concentrations (M) of the isomers were the following: P2 (0.0034), P3 (0.0036), P4 (0.0013), P5 (0.012), P6 (0.0003), P7 (0.0008), P8 (0.0004), P9 (0.0002), P10 (0.0009), and P11 (0.0004); yield was 9% (TON = 47). It can be clearly seen that the ratio of isomeric alcohols in the case of this catalytic system (a, b) is different from that
obtained earlier for other catalysts (c–f). Indeed, concentrations of isomers P8 and P9 is noticeably low in comparison with amounts of both P6, P7 and P10, P11. This effect has not been found for other catalysts (c–f) and is apparently due to sterical hindrance around catalytic centers in 1. Like in the cyclohexane oxidation, chromatograms of oxygenates obtained from methylcyclohexane (Figure 6a,b) before and after reduction with PPh3 are very similar and this indicates that alkyl hydroperoxides are also not formed in this experiment.

Table 1. Oxidation of cyclohexane with m-CPBA catalyzed by complex 1 1.

| Entry | Time (min) | Reduction with PPh3 | Cyclohexanone (M) at 20 °C | Cyclohexanol (M) at 20 °C |
|-------|------------|---------------------|---------------------------|--------------------------|
| 1     | 120        | no                  | 0.007                     | 0.007                    |
| 2     | 15         | yes                 | 0.005                     | 0.006                    |
| 3     | 300        | no                  | 0.009                     | 0.006                    |
| 4     |             | yes                 | 0.008                     | 0.007                    |

| Entry | Time (min) | Reduction with PPh3 | Cyclohexanone (M) at 50 °C | Cyclohexanol (M) at 50 °C |
|-------|------------|---------------------|---------------------------|--------------------------|
| 5     | 7          | no                  | 0.008                     | 0.02                     |
| 6     | 15         | yes                 | 0.007                     | 0.017                    |
| 7     | 15         | no                  | 0.009                     | 0.022                    |
| 8     | 15         | yes                 | 0.009                     | 0.023                    |
| 9     | 15         | yes                 | 0.0002                    | 0.0003                   |
| 10    | 15         | no                  | 0.0005                    | 0.0027                   |
| 11    | 15         | yes                 | 0.00004                   | 0.000007                 |
| 12    | 30         | no                  | 0.009                     | 0.022                    |
| 13    | 30         | yes                 | 0.009                     | 0.022                    |
| 14    | 30         | yes                 | 0.0007                    | 0.0007                   |
| 15    | 30         | no                  | 0.0005                    | 0.002                    |
| 16    | 60         | no                  | 0.009                     | 0.023                    |
| 17    | 60         | yes                 | 0.009                     | 0.023                    |
| 18    | 60         | yes                 | 0.001                     | 0.001                    |

1 Conditions. Concentrations [1]0 = 5 × 10−4 M, [cyclohexane]0 = 0.46 M, [m-CPBA]0 = 0.13 M. Solvent MeCN, total volume of the reaction solution was 5 mL; 2 For this entry, TON = 64, TOF = 256 h−1; 3 Salt Ni(NO3)2 was used instead of catalyst 1; 4 An experiment in the absence of any Ni compound.

![Diagram](image-url)

Figure 5. Products formed in the methylcyclohexane oxidation.
The oxidation of cis-1,2-dimethylcyclohexane with m-CPBA in MeCN catalyzed complex 1 proceeds non-stereoselectively: the ratio of formed tertiary trans and cis alcohols t/c was 0.88 before reduction with PPh₃ and 0.93 after the reduction (yield was 12% based on cis-1,2-DMCH; TON = 34). In the blank experiment (without complex 1) the t/c ratio was 0.77 after reduction with PPh₃ (yield was 5%).

3. Materials and Methods

3.1. Synthesis of Compound 1

Compound PhSi(OEt)₃ and solvents were purchased from Acros Organics (Moscow, Russia) and were used as received.

Compound PhSi(OEt)₃ (3 g, 12.48 mmol), water (0.45 g, 24.96 mmol) and NaOH (0.5 g, 12.50 mmol) in 20 mL of methanol were placed into a flask, equipped with a magnetic stirrer and condenser. After total dissolution of NaOH, the solution was heated to reflux for 1.5 h. Afterwards solution was cooled down to room temperature and mixed with 85 mL of dioxane. Then Ni(NH₃)₆Cl₂ (1.4 g, 6.04 mmol) was added at once. Mixture was brought to reflux along with simultaneous distillation of the solution to remove methanol from reaction mixture. When 18 mL of distillate was collected, mixture was heated to reflux for additional 4 h and then left stirring at room temperature overnight. Then reaction mixture was filtered into an evaporation flask containing benzonitrile (8 mL). The flask was equipped with a septum and needle to allow solvents to evaporate under a slow current of nitrogen. Immediately after yellow-colored crystals began to form, the flask was transferred to the fridge and stored there until the crystal fraction growth (two weeks) ceased, as visually determined.
A few selected single crystals were used for the X-ray study (for details, see below). Yield: 0.41 g, 20%; elemental analysis calcd (%) for \([\text{PhSiO}_{1.5}]_{12}\text{(NiO)}_6\text{(NaCl)}\): Ni 17.12, Si 16.39, C 42.04, H 2.94, N 0; found (in a vacuum-dried sample): Ni 17.01, Si 16.30, C 42.64, H 3.07, N traces.

3.2. X-ray Diffraction Study

X-ray diffraction studies were carried out on Bruker APEX DUO diffractometer (Madison, WI, USA). The structure was solved by direct method and refined in anisotropic approximation against F2. The positions of hydrogen atoms were calculated from geometrical point of view and refined in isotropic approximation (the C-H and O-H distances and displacement parameters of hydrogen atoms are constrained). All calculations were carried out with SHELX (Gottingen, Germany) [54,55] and OLEX2 software (Durham, UK) [56]. The experimental parameters and crystal data are summarized in Table 2.

| Brutto Formula | C_{138}H_{174}ClN_{2}NaNi_{6}O_{52}Si_{12} |
|---------------|------------------------------------------|
| Formula weight| 3437.54                                   |
| T, K          | 120                                       |
| Space group   | P2\,\_\,n                                 |
| Z             | 2                                         |
| a, Å          | 16.1899 (12)                              |
| b, Å          | 18.2778 (14)                              |
| c, Å          | 27.093 (2)                                |
| β, °          | 101.513 (2)                               |
| V, Å³         | 7855.9 (10)                               |
| d_{calc}, g/cm³ | 1.456                                    |
| μ, cm⁻¹      | 9                                         |
| F(000)        | 3600                                      |
| 2θ_{max}, °   | 50                                        |
| Reflections collected | 100,379                             |
| Independent reflections | 23,101                               |
| Reflections with I > 2σ(I) | 11,161                                 |
| Parameters   | 942                                       |
| R1 [for refl. with I > 2σ(I)] | 0.0823                                   |
| wR2          | 0.2050                                    |
| GOF          | 1.006                                     |
| Residual electron density, e- Å⁻³(ρ_{min}/ρ_{max}) | 2.600/−2.575 |

3.3. Catalytic Oxidation of Alkanes and 1-Phenylethanol

Typically, the catalyst and the co-catalyst (nitric or trifluoroacetic acid) were introduced into the reaction mixture in the form of stock solutions in acetonitrile. The reactions of alcohols and hydrocarbons were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring and using MeCN as solvent. The substrate (alcohol or hydrocarbon) was then added and the reaction started when the oxidant was introduced in one portion (CAUTION: the combination of air or molecular oxygen and peroxides with organic compounds at elevated temperatures may be explosive!). The reactions with 1-phenylethanol were analyzed by \(^1\)H-NMR method (solutions in acetone-\(d_6\); “Bruker AMX-400” instrument, 400 MHz, Billerica, MA, USA). Areas of methyl group signals were measured to quantify oxygenates formed in oxidations of 1-phenylethanol. As stated previously, the samples obtained in the alkane oxidation were typically analyzed twice (before and after their treatment with PPh₃) by GC. This method (an excess of solid triphenylphosphine is added to the samples 10–15 min before the GC analysis) was proposed by one of us earlier [48–51]. Samples of the reaction mixture were analyzed by GC (Agilent 6890, Santa Clara, California, United States, N₂ was carrier gas, FID) and GC-MS (Shimadzu QP-2010 Plus, Nishinokyo-Kuwabara-cho, Nakagyo-ku, Kyoto 604-8511, Japan; He was carrier gas); in both instruments the column was BP-20 (SGE; polyethylene glycol...
Molecules 2016, 21, 665

Assignment of peaks was made by comparison with chromatograms of authentic samples and by GC-MS.

4. Conclusions

Synthesized in this work complex (PhSiO1.5)12(NiO)6(NaCl)(C4H8O2)13(PhCN)2(H2O)2 represents very rare case of polyhedral complexation of metallasilsesquioxane with benzonitrile. The complex exhibited catalytic activity in oxidation of alcohols with tert-butylhydroperoxide and alkanes with meta-chloroperoxybenzoic acid.

Supplementary Materials: Supplementary materials can be accessed at: http://www.mdpi.com/1420-3049/21/5/665/s1. CCDC 1471551 contains the supplementary crystallographic data for complex 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments: The authors gratefully acknowledge support of the Russian Foundation for Basic Research (projects 14-03-00713, 16-03-00206, 16-03-00254) and the “Science without Borders Program, Brazil–Russia”, CAPES (grant A017-2013). D.M. is grateful to CNPq (grants 311585/2013-2, 472130/2012-9).

Author Contributions: A.N.B., M.M.L., E.S.S. and G.B.S. conceived and designed experiments on synthesis and catalytic application of compound 1, A.I.Y. made synthesis of 1, I.S.S. and D.M. performed experiments on oxidations and analysis of products, A.A.K., A.V.V. and M.A.E. carried out X-ray experiments, their analysis and topological analysis. A.N.B. and G.B.S. wrote the paper. Authors disclosed no actual or potential conflict of interest, and have approved the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Murugavel, R.; Voigt, A.; Walawalkar, M.G.; Roesky, H.W. Hetero- and Metallasiloxanes Derived from Silanediols, Disilanols, Silanetriols, and Trisilanols. Chem. Rev. 1996, 96, 2205–2236. [CrossRef] [PubMed]
2. Lorenz, V.; Fischer, A.; Gießmann, S.; Gilje, J.W.; Gun’ko, Y.; Jacob, K.; Edelmann, F.T. Disiloxanediolates and polyhedral metallasilsesquioxanes of the early transition metals and f-elements. Coord. Chem. Rev. 2000, 206–207, 321–368. [CrossRef]
3. Hanssen, R.W.J.M.; van Santen, R.A.; Abbenhuis, H.C.L. The Dynamic Status Quo of Polyhedral Silsesquioxane Coordination Chemistry. Eur. J. Inorg. Chem. 2004, 675–683. [CrossRef]
4. Roesky, H.W.; Anantharaman, G.; Chandrasekhar, V.; Jancik, V.; Singh, S. Control of Molecular Topology and Metal Nuclearity in Multimetallic Assemblies: Designer Metallosiloxanes Derived from Silanetriols. Chem. Eur. J. 2004, 10, 4106–4114. [CrossRef] [PubMed]
5. Lorenz, V.; Edelmann, F.T. Metallasilsesquioxanes. Adv. Organomet. Chem. 2005, 53, 101–153.
6. Jutzi, P.; Lindemann, H.M.; Nolte, J.-O.; Schneider, M. Synthesis, Structure, and Reactivity of Novol Oligomeric Titanasiloxanes. In Silicon Chemistry: From the Atom to Extended Systems; Jutzi, P., Schubert, U., Eds.; Wiley: Weinheim, Germany, 2007; pp. 372–382.
7. Edelmann, F.T. Metallasilsesquioxanes. Synthetic and Structural Studies. In Silicon Chemistry: From the Atom to Extended Systems; Jutzi, P., Schubert, U., Eds.; Wiley: Weinheim, Germany, 2007; pp. 383–394.
8. Ward, A.J.; Masters, A.F.; Maschmeyer, T. Metallasilsesquioxanes: Molecular Analogues of Heterogeneous Catalysts. Adv. Silicon Sci. 2011, 3, 135–166.
9. Levitsky, M.M.; Bilyachenko, A.N. Modern concepts and methods in the chemistry of polyhedral metallasiloxanes. Coord. Chem. Rev. 2016, 306, 235–269. [CrossRef]
10. Schax, F.; Bill, E.; Herwig, C.; Limberg, C. Dioxygen Activation by Chromium(II)- and Chromium(IV)-Siloxide Complexes. Angew. Chem. Int. Ed. 2014, 53, 12741–12745. [CrossRef] [PubMed]
11. Korlyukov, A.A.; Eskova, M.A.; Tkachenko, I.M.; Kononevich, Y.N.; Shchegolikhina, O.I.; Muzafarov, A.M. Heteroligand nickel siloxane with 4-vinylbenzyl substituents. Mendeleev Commun. 2015, 25, 226–228. [CrossRef]
12. Anisimov, A.A.; Kononevich, Y.N.; Zhemchugov, P.V.; Milenin, S.A.; Korlyukov, A.A.; Tsareva, U.S.; Peregudov, A.S.; Dorovatovskii, P.V.; Molodtsova, Y.A.; Takazova, R.U.; et al. Synthesis and structure of new polyhedral Ni, Na- and Cu, Na-metallasiloxanes with tolyl substituent at the silicon atom. RSC Adv. 2016, 6, 22052–22060. [CrossRef]
Balamurugan, M.; Mayilmurugan, R.; Suresh, E.; Palaniandavar, M. Nickel(II) complexes of tripodal 4N ligands as catalysts for alkane oxidation using m-CPBA as oxidant: Ligand stereoelectronic effects on catalysis. Dalton Trans. 2011, 40, 9413–9424. [CrossRef] [PubMed]

Hikichi, S.; Hanau, K.; Fujimura, T.; Okuda, H.; Nakazawa, J.; Ozhu, Y.; Kobayashi, C.; Akita, M. Characterization of nickel(II)-acylperoxo species relevant to catalytic alkane hydroxylation by nickel complex with mCPBA. Dalton Trans. 2013, 42, 3346–3356. [CrossRef] [PubMed]

Tordin, E.; List, M.; Monkwius, U.; Schindler, S.; Knör, G. Synthesis and characterisation of cobalt, nickel and copper complexes with tripodal 4N ligands as novel catalysts for the homogeneous partial oxidation of alkanes. Inorg. Chim. Acta 2013, 402, 90–96. [CrossRef] [PubMed]

Mehta, A.; Stephen, S.; Tembo, G. Catalytic oxyfunctionalization of alkanes and alkenes by hetero-metal Mn-Cu and Mn-Ni clusters. Indian J. Chem. 2014, 53, 1500–1504.

Sankaralingam, M.; Balamurugan, M.; Palaniandavar, M.; Vadiivelu, P.; Suresh, C.H. Nickel(II) complexes of pentadentate N5 ligands as catalysts for alkane hydroxylation by using m-CPBA as oxidant: A combined experimental and computational study. Chem. Eur. J. 2014, 20, 11346–11361. [CrossRef] [PubMed]

Silva, T.F.S.; Rocha, B.G.M.; Guedes Da Silva, M.F.C.; Martins, L.M.D.R.S.; Pombeiro, A.J.L.; V(I), Fe(II), Ni(II) and Cu(II) complexes featuring 2,2,2-tris(pyrazol-1-y1)ethyl methanesulfonate: Application as catalysts for the cyclooctane oxidation. New J. Chem. 2016, 40, 528–537. [CrossRef]

Pathan, S.; Patel, A. Solvent free clean selective oxidation of alcohols catalyzed by mono transition metal (Co, Mn, Ni) substituted Keggin-phosphomolybdates using hydrogen peroxide. Appl. Catal. A Gen. 2013, 459, 59–64. [CrossRef]

Adam, F.; Wan-Ting, O. Nickel porphyrin hybrid material based on functionalised silica for the selective oxidation of benzyl alcohol. J. Phys. Sci. 2013, 24, 1–19.

Arion, V.B.; Platzer, S.; Rapta, P.; Machata, P.; Breza, M.; Vegh, D.; Dunsch, L.; Telser, J.; Shova, S.; Mac Leod, T.C.O.; et al. Marked stabilization of redox states and enhanced catalytic activity in galactose oxidase models based on transition metal S- methylimidoxoselenocarbonates with -SR group in ortho position to the phenolic oxygen. Inorg. Chem. 2013, 52, 7524–7540. [CrossRef] [PubMed]

Sarma, K.; Devi, N.; Kalita, M.; Sarma, B.; Barman, P. Nickel(II), copper(II), cobalt(II), and palladium(II) complexes with a Schiff base: Crystal structure, DFT study and copper complex catalyzed aerobic oxidation of alcohol to aldehyde. J. Coord. Chem. 2015, 68, 3685–3700. [CrossRef]

Kosheleva, A.M.; Maksimov, N.G.; Kornienko, G.V.; Kornienko, V.L. Studies of kinetics of indirect in situ electrocatalytic oxidation of aliphatic alcohols to carboxylic acids by active forms of oxygen. Russ. J. Electrochem. 2015, 51, 1079–1085. [CrossRef]

Urgoitia, G.; Sammartin, R.; Herrero, M.T.; Domínguez, E. An outstanding catalyst for the oxygen-mediated oxidation of arylcarbinols, arylmethylene and arylacetylene compounds. Chem. Commun. 2015, 51, 4799–4802. [CrossRef] [PubMed]

Fu, Y.; Sun, L.; Yang, H.; Xu, L.; Zhang, F.; Zhu, W. Visible-light-induced aerobic photocatalytic oxidation of aromatic alcohols to aldehydes over Ni-doped NH2-MIL-125(Ti). Appl. Catal. B Environ. 2016, 187, 212–217. [CrossRef]

Lindsay Smith, J.R.; Shul’pin, G.B. Efficient stereoselective oxygenation of alkanes by peroxycacidic acid or hydrogen peroxide and acetic acid catalysed by a manganese(IV) 1,4,7-trimethyl-1,4,7-triazacyclononane complex. Tetrahedron Lett. 1998, 39, 4909–4912. [CrossRef]

Shul’pin, G.B.; Lindsay-Smith, J.R. Oxidations by the reagent ‘H2O2-manganese(IV) complex-carboxylic acid’. Part 1. Oxidation of saturated hydrocarbons with peroxo acids and hydrogen peroxide. Russ. Chem. Bull. 1999, 47, 2379–2386. [CrossRef]

Shul’pin, G.B.; Stoeckl-Evans, H.; Mandelli, D.; Kozlov, Y.N.; Tesouro Vallina, A.; Woitiski, C.B.; Jimenez, R.S.; Carvalho, W.A. Oxidation of alkanes with m-chloroperbenzoic acid catalyzed by iron(III) chloride and a polydentate amine. J. Mol. Catal. A: Chem. 2004, 219, 255–264. [CrossRef]

Shul’pin, G.B. Metal-catalysed hydrocarbon oxygenations in solutions: The dramatic role of additives: A review. J. Mol. Catal. A Chem. 2002, 189, 39–66. [CrossRef]

Shul’pin, G.B. Selectivity enhancement in functionalization of C–H bonds: A review. Org. Biomol. Chem. 2010, 8, 4217–4228. [CrossRef] [PubMed]
50. Shul’pin, G.B. C–H functionalization: Thoroughly tuning ligands at a metal ion, a chemist can greatly enhance catalyst’s activity and selectivity. Perspective. *Dalton Trans.* 2013, 42, 12794–12818. [CrossRef] [PubMed]

51. Shul’pin, G.B. New Trends in Oxidative Functionalization of Carbon–Hydrogen Bonds: A Review. *Catalysts* 2016, 6, 50. [CrossRef]

52. Kirillova, M.V.; Kirillov, A.M.; Mandelli, D.; Carvalho, W.A.; Pombeiro, A.J.L.; Shul’pin, G.B. Mild homogeneous oxidation of alkanes and alcohols including glycerol with tert-butyl hydroperoxide catalyzed by a tetracopper(II) complex. *J. Catal.* 2010, 272, 9–17. [CrossRef]

53. Vinogradov, M.M.; Shul’pina, L.S.; Kozlov, Y.N.; Kudinov, A.R.; Ikonnikov, N.S.; Shul’pin, G.B. Oxidation of hydrocarbons and alcohols with peroxides catalyzed by new π-cymene osmium complexes. *J. Organomet. Chem.* 2015, 784, 52–61. [CrossRef]

54. Sheldrick, G.M. A Short History of SHELX. *Acta Cryst.* 2008, A64, 112–122. [CrossRef] [PubMed]

55. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* 2015, C71, 3–8.

56. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* 2009, 42, 339–341. [CrossRef]

**Sample Availability:** A sample of the compound 1 is available from the authors.

© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (http://creativecommons.org/licenses/by/4.0/).