Dioxomolibdenum(VI) complexes with thiosemicarbazone ligands as (pre)catalysts for olefin epoxidation

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DIOXOMOLYBDENUM(VI) COMPLEXES WITH THIOSEMICARBAZONE LIGANDS AS (PRE)CATALYSTS FOR OLEFIN EPOXIDATION

Diploma Thesis

submitted to the Department of Chemistry,
Faculty of Science, University of Zagreb
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Zagreb, 2019.

This Diploma Thesis was performed at Division of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb under mentorship of Professor Višnja Vrdoljak, under assistant mentorship of Dr. Jana Pisk and at the Laboratory of Coordination Chemistry of the National Center for Scientific Research in Castres, under mentorship of Associate professor Dominique Agustin.

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ABSTRACT

DIOXOMOLYBDENUM(VI) COMPLEXES WITH THIOSEMICARBAZONE LIGANDS AS (PRE)CATALYSTS FOR OLEFIN EPOXIDATION

Sanja Renka

Three polynuclear dioxomolybdenum(VI) complexes $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$, $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$ and $[\{MoO_2(5\text{-}MeO\text{-}SalTSC)\}\cdot\frac{1}{2}CH_3CN]_n$, two mononuclear $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$ and $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]\cdot MeOH$ and hybrid organic-inorganic POM complex $[MoO_2(H5MeO\text{-}SalTSC\text{-}4Me)(CH_3CN)]_2Mo_6O_{19}$ have been synthesized by the reaction of $[MoO_2(acac)_2]$ and corresponding thiosemicarbazone ligand in 1:1 and 7:1 molar ratio, respectively. Mononuclear complexes were obtained from a methanolic solution, whereas polynuclear and POM hybrid complex from acetonitrile. Complexes were characterized by the IR spectroscopy, elemental and thermogravimetric analysis. Additionally, molecular and crystal structures of mononuclear complexes were determined by the single crystal X-ray diffraction. Catalytic activity of all complexes was tested in the solvent-free epoxidation of *cis*-cyclooctene, cyclohexene and (*R*)-limonene with TBHP as an oxidant and low catalyst loading (0.05 %).

(73 pages, 26 figures, 6 schemes, 7 tables, 30 references, original in English)

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SAŽETAK

TIOSEMIKARBAZONSKI KOMPLEKSI DIOKSOMOLIBDENA(VI) KAO (PRED)KATALIZATORI U REAKCIJAMA EPOKSIDACIJE OLEFINA

Sanja Renka

Reakcijom $[MoO_2(acac)_2]$ i odgovarajućeg tiosemikarbazonskog liganda u 1:1 odnosno 1:7 molarnom omjeru pripravljeni su kompleksni spojevi molibdena(VI): polinuklearni $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$, $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$ i $[\{MoO_2(5\text{-}MeO\text{-}SalTSC)\}\cdot\frac{1}{2}CH_3CN]_n$, mononuklearni $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$ i $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]\cdot MeOH$ te hibridni organsko-anorganski polioksomolibdatni spoj $[MoO_2(H5MeO\text{-}SalTSC\text{-}4Me)(CH_3CN)]_2Mo_6O_{19}$. Mononuklearni kompleksi dobiveni su iz metanolne otopine, a polinuklearni i hibridni iz acetonitrila. Kompleksi su identificirani IR spektroskopijom, elementnom i termogravimetrijskom analizom te je dodatno, difrakcijom rentgenskog zračenja na monokristalnom uzorku, određena molekulska i kristalna struktura mononuklearnih kompleksa. Katalitička aktivnost pripravljenih spojeva ispitana je u reakcijama epoksidacije olefina (*cis*-ciklooktena, cikloheksena i (*R*)-limonena) s TBHP-om u uvjetima bez otapala. Za epoksidaciju je korišteno 0,05 % katalizatora u odnosu na supstrat.

(73 stranica, 26 slika, 6 shema, 7 tablica, 30 literaturnih navoda, jezik izvornika: engleski)

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Ključne riječi: kompleksi molibdena(VI), polioksomolibdati, tiosemikarbazoni, epoksidacija bez dodatka organskog otapala

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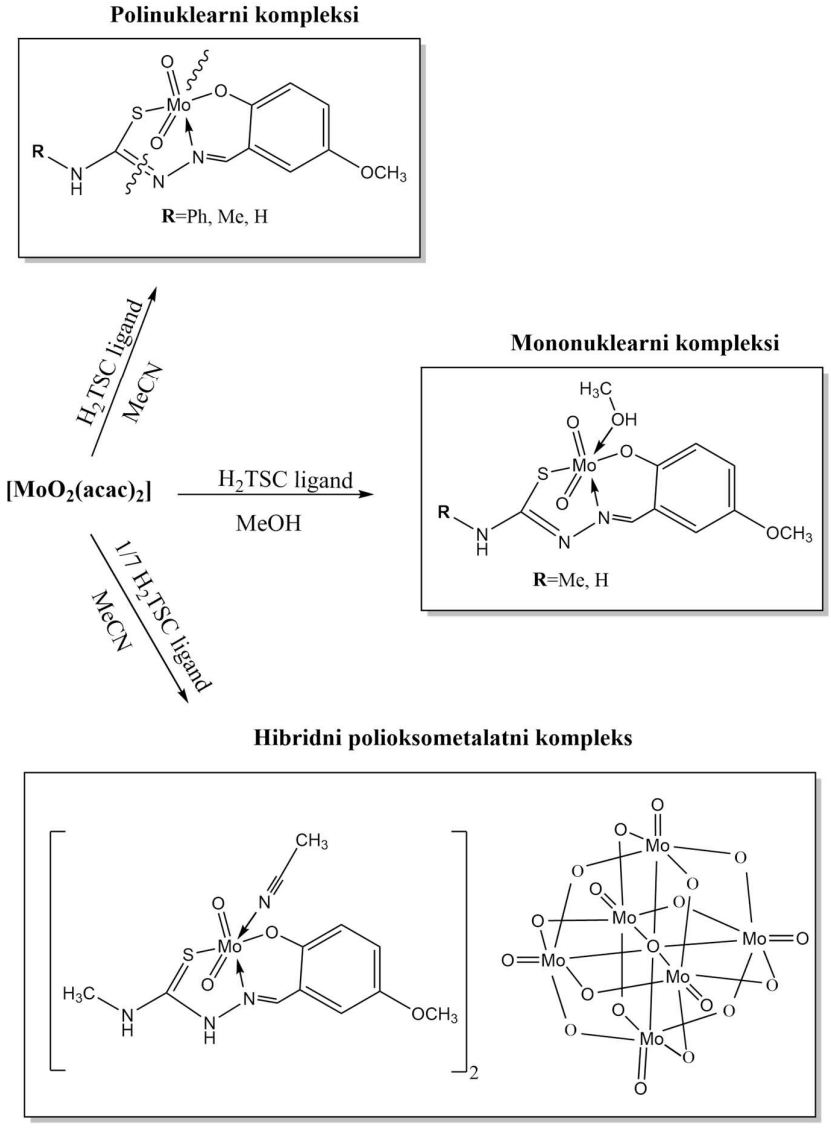
PROŠIRENI SAŽETAK

Istraživanje kompleksnih spojeva dioksomolibdena(VI) potaknuto je pronalaskom molibdoenzima koji kataliziraju biološke reakcije i sadrže *cis*-$\{MoO_2\}^{2+}$ jezgru u aktivnom mjestu. U svrhu oponašanja katalitički aktivnog mjesta enzima, najčešće su sintetizirani kompleksi dioksomolibdena(VI) s ligandima koji sadrže donorne atome kisika, dušika i/ili sumpora. Posebno interesantni su *ONS*-tiosemikarbazonski ligandi zbog jednostavne priprave, stabilnosti i mogućnosti koordinacije na metalne centre. Kompleksi spojevi molibdena i tiosemikarbazona najčešće su mononuklearni, dinuklearni i polinuklearni. Kod mononuklearnih kompleksa šesto koordinacijsko mjesto zauzima molekula otapala, a kod dinuklearnih i polinuklearnih kompleksa kisikov atom MoO_2^{2+} jezgre iz susjedne molekule. Polioksomolibdati su polianionske struktre sastavljene od povezanih MO_n poliedra među kojima je primjerice heksamolibdat $\{Mo_6O_{19}\}^{2-}$ još zvan Lindqvistov anion. Kompleksni kationi mogu kompenzirati negativni naboj polioksomolibdatnog aniona tvoreći hibridne polioksomolibdatne spojeve.

Mo(VI) spojevi imaju katalitički primjenu u različitim industrijskim procesima kao što je epoksidacija olefina. Radi potrebe za razvitkom ekološki čišće i ekonomičnije proizvodnje, sintetiziraju se različiti katalizatori aktivni u uvjetima bez organskih otapala. Najčešći supstrati za testiranje katalizatora u reakcijama epoksidacije su *cis*-ciklookten, cikloheksen i (*R*)-limonen. Njihovi produkti reakcije tj. epoksidi važni intermedijeri u organskoj sintezi lijekova, prehrambenih aditiva, boja, parfema itd.

U ovom diplomskom radu priređeni su tiosemikarbazonski ligandi kondenzacijom 5-metoksi-2-hidroksibenzaldehida s 4-fenil-3-tiosemikarbazidom, 4-metil-3-tiosemikarbazidom odnosno tiosemikarbazidom u metanolnoj otopini uz refluks. Polinuklearni i mononuklearni kompleksi molibdena(VI) $[MoO_2(5\text{-MeO-SalTSC-4-Ph})]_n$, $[MoO_2(5\text{-MeO-SalTSC-4-Me})]_n$, $[\{MoO_2(5\text{-MeO-SalTSC})\}\cdot\frac{1}{2}CH_3CN]_n$, $[MoO_2(5\text{-MeO-SalTSC-4-Me})(MeOH)]$ i $[MoO_2(5\text{-MeO-SalTSC})(MeOH)]\cdot MeOH$ priređeni su reakcijom $[MoO_2(acac)_2]$ i odgovarajućeg prethodno pripravljenog liganda (1:1 molarni omjer), u otopini acetonitrila odnosno metanola i uz refluks (Shema 1). Stajanjem pri sobnoj temperaturi kompleksi $[\{MoO_2(5\text{-MeO-}$

SalTSC)}·½$CH_3CN]_n$ i [MoO_2(5MeO-SalTSC)(MeOH)]·MeOH gube kristaliziranu molekulu otapala te su analizirani kao [MoO_2(5MeO-SalTSC)(MeOH)]$_n$ i [MoO_2(5MeO-SalTSC)(MeOH)]. Hibridni spoj kompleksnog kationa molibdena(VI) i Lindqvistnog aniona [MoO_2(5MeO-SalTSC-4-Me)(CH_3CN)]$_2Mo_6O_{19}$ dobiven je reakcijom [$MoO_2(acac)_2$] i 5-MeO-SalTSC-4-Me liganda u molarnom omjeru 7:1, u otopini acetonitrila uz blago zagrijavanje (Shema 1).



Shema 1. Prikaz dobivenih polinuklearnih i mononuklearnih molibdenovih kompleksa te hibridnog kompleksa s kompleksnim molibdenovim kationom i Lindqvistovim anionom.

Izolirani kompleksi identificirani su infracrvenom spektroskopijom te elementnom i termogravimetrijskom analizom, a molekulska i kristalna struktura mononuklearnih kompleksa određena je difrakcijom rentgenskih zraka na jediničnom kristalu. Infracrvenom spektroskopijom ustanovljena je razlika između mononukelarnih i polinuklearnih kompleksa te je utvrđeno postojanje vrpca karakterističnih za istezanje C=N imino i C–O fenilne veze. U spektrima mononuklearnih kompleksa opažene su dvije apsorpcijske vrpce istezanja MoO_2^{2+} jezgre, a kod polinuklearnih kompleksa intenzivna vrpca istezanja Mo=O···Mo premošćujuće skupine. U IR spektru hibridnog polioksomolibdatnog kompleksa vidljive su karakteristične vrpce istezanja M=O terminalne i premošćujuće skupine polioksomolibdatnog aniona. Prema podatcima termogravimetrijske analize, teorijski udjeli molibdena i molekula otapala u kompleksima su u skladu s eksperimentalno dobivenima. Difrakcijom rentgenskih zraka na jediničnom kristalu dodatno je potvrđena struktura mononuklearnih kompleksa.

Pripravljenim kompleksnim spojevima ispitana je katalitička aktivnost u reakciji epoksidacije *cis*-ciklooktena, cikloheksana i (*R*)-limonena bez dodatka otapala i uz *tert*-butil hidroperoksid (TBHP) kao oksidans. Cilj katalitičkog ispitivanja bio je odrediti utjecaj: a) supstituenta, b) tipa kompleksa (polinuklearni, mononuklearni i hibridni polioksomolibdatni) i c) dodatka metanola u reakcijama s polinuklearnim kompleksima. Postupak se sastojao od dodatka supstrata, acetofenona i molibdenova(VI) kompleksa nakon čega je reakcijska smjesa zagrijana do 80 ˚C te je dodan TBHP. Molarni omjer katalizatora, olefina i TBHP-a iznosio je 0,01:20:40 za mononuklearne i polinukelarne komplekse te 0,005:20:40 za hibridni polioksomolibdatni kompleks. Također, ispitan je utjecaj dodatka male količine metanola u reakcijama epoksidacije ciklooktena s polinuklearnim kompleksima. Reakcije su praćene 6 sati i za to vrijeme su, u određenim vremenskim intervalima, uzimani alikvoti organske faze i analizirani plinskom kromatografijom. Pretvorbe reaktanata i produkata određene su prema njihovim kalibracijskim krivuljama u odnosu na acetofenon kao unutarnji standard.

Katalitičke reakcije epoksidacije olefina bile su uspješne uzimajući u obzir male količine korištenog katalizatora (0,05 %). Molibdenovi katalizatori pokazali su se najefikasniji u epoksidaciji *cis*-ciklooktena. Konverzija ciklooktena u slučaju polinuklearnih i mononuklearnih kompleksa iznosila je 77-85 %, dok je za hibridni polioksomolibdatni kompleks iznosila visokih 94%. Budući da je oksid bio jedini produkt reakcije epoksidacije ciklooktena, selektivnost je također bila vrlo visoka (90 %). Epoksidacija cikloheksena dala je

nešto lošije rezultate. Razlog tomu je brza hidroliza nastalog cikloheksen oksida u *trans*-cikloheksen-1,2-diol zbog čega je selektivnost za sve komplekse iznosila manje od 6 %. Konverzija supstrata bila je dobra (oko 70 %), a za hibridni polioksomolibdatni kompleks i vrlo dobra 88%. Zbog nastanka velike količine diola i ostalih produkata, epoksidacija (*R*)-limonena pokazala je najniže vrijednosti selektivnosti (<1 %). Ipak, konverzije su bile dobre (58-83 %).

Budući da su kompleksi s različitim supstituentima pokazali vrlo slične rezultate, zaključeno je da ligandi nemaju značajan utjecaj na katalizu. Isto tako, dodatak metanola u reakcije epoksidacije ciklooktena s polinuklearnim kompleksima nije uzrokovao značajnu razliku zbog čega takvi eksperimenti na ostalim supstratima nisu bili provedeni. Uzimajući u obzir vrstu molibdenova kompleksa, hibridni polioksomolibdatni kompleks pokazao se kao najbolji. Takav rezultat bio je očekivan budući da hibridni polioksomolibdatni kompleks sadrži dva potencijalna aktivna mjesta za katalizu, $[MoO_2(HL^2)]^+$ kation i $Mo_6O_{19}^{2-}$ anion.

§ 1. INTRODUCTION

Molybdenum has been found in the active sites of some enzymes and plays a very important role in biological systems. For example, xanthine oxidase and sulfite oxidase catalyze oxygen atom transfer reactions and contain molybdenum atom coordinated by two oxo ligands and two or three thiol ligands.[1] Nowadays, in order to mimic the coordination environment of active sites, dioxomolybdenum(VI) complexes with thio ligands are continuously studied.[2-4]

Reactions of tridentate thiosemicarbazone ligands and *cis*-$\{MoO_2\}^{2+}$ containing compounds usually result in the formation of mononuclear, dinuclear and polynuclear complexes. In presence of the labile sixth coordination site, suitable for the substrate activation, these complexes can be used as a catalysts in industry.[5] This includes the olefin epoxidation reactions in order to produce epoxides that are important in the synthesis of pharmaceuticals, food additives, fine chemicals and other. For the industrial processes, implementation of green chemistry principles is of great interest and molybdenum complexes were shown to be very efficient under the solvent-free conditions.[5-7]

The goal of this diploma thesis was: a) synthesis and structural characterization of dioxomolybdenum(VI) complexes with different thiosemicarbazone ligands and b) testing of obtained complexes as a (pre)catalyst for the epoxidation of olefins under solvent-free conditions. In the reaction of starting $[MoO_2(acac)_2]$ complex and thiosemicarbazone ligands in 1:1 molar ratio, mononuclear and polynuclear complexes were obtained, while 7:1 molar ratio was leading to the hybrid organic-inorganic polyoxomolybdate complex. Mononuclear complexes were synthesised in the methanolic solution whereas polynuclear and POM hybrid in acetonitrile. All the complexes were characterized by the IR spectroscopy, elemental and thermogravimetric analysis. In addition, molecular and crystal structures of mononuclear complexes were determined by the X-ray diffraction. Catalytic epoxidation reactions of *cis*-cyclooctene, cyclohexene and (*R*)-limonene were conducted in the solvent-free conditions with TBHP as an oxidant and monitored by the gas-chromatography (GC).

§ 2. LITERATURE REVIEW

2.1. Thiosemicarbazone ligands

Thiosemicarbazones of general formula $R^1R^2C^2{=}N^3{-}N^2(H){-}C^1(=S)N^1R^3R^4$ (Figure 1) are very interesting because of their applications and biological properties (determination of the trace metals, inhibition of the corrosion, antibacterial, antifungal and antitumor properties *etc*.).[8]

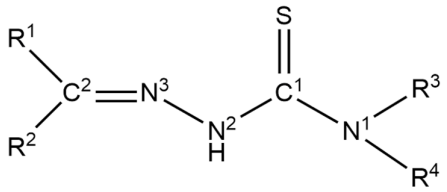


Figure 1. The basic structure of thiosemicarbazone.

Thiosemicarbazones can be synthesized by the conventional solution-based method and/or microwave-assisted method, both involving the condensation of aldehyde or ketone with thiosemicarbazide (example shown in Figure 2). The most common synthetic method is the condensation of aldehyde and thiosemicarbazide in alcohol as a solvent. However, the microwave-assisted solvent-free method seems to be more efficient, safe and environmentally friendly.[9]

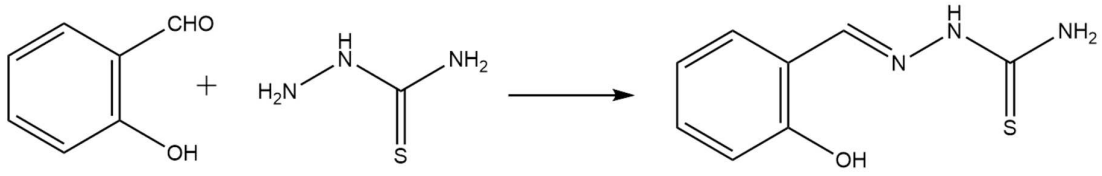


Figure 2. Synthesis of a salicylaldehyde thiosemicarbazone.

The basic structure of thiosemicarbazones is shown in Figure 1. If thiosemicarbazone is derived from an aldehyde, R^1 is a hydrogen atom and R^2 can be alkyl, aryl or heterocyclic group. If derived from a ketone, both substituents are alkyl or aryl groups (different or identical). Moreover, in the case of cyclopentanone thiosemicarbazone, the ketone is cyclic

(C^2 carbon is part of the ring). Similarly, the N^1 nitrogen atom can be part of the ring or substituents R^3 and R^4 are both hydrogen atoms or one substituent is a hydrogen atom and the other one is alkyl or aryl group.[8]

Due to the intramolecular proton transfer, these compounds can exist as thione/thiol tautomeric forms (Figure 3).[1]

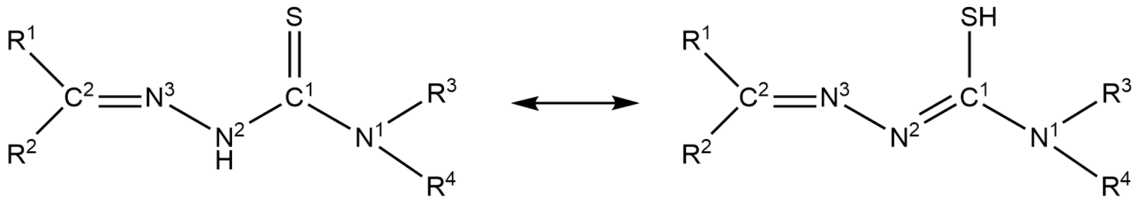


Figure 3. Thione and thiol tautomeric forms of thiosemicarbazones.

These ligands can bind in neutral or anionic form, the second one being generated after a loss of $-N^2H$ or $-SH$ hydrogen atom from ligand in thione and thiol form, respectively. Good chelating capacity can be further increased by inserting an additional functional group to the aldehyde part.

In the neutral form, thiosemicarbazones can bind as a monodentate, bidentate and tridentate ligand. The ligand binds as monodentate through the sulphur atom (Figure 4a) or sulphur atom is bridging two metal centres (Figure 4b). In bidentate coordination, the binding occurs via sulphur and nitrogen atoms as N^3S-chelation (Figure 4c) or N^3S-chelation with bridging sulphur atom (Figure 4d). However, additional donor atom (X) can provide tridentate coordination modes: XN^3S-chelation (Figure 4e), XN^3S-chelation with bridging sulphur atom (Figure 4f) and XN^3S-chelation with bridging donor atom X (Figure 4g).[8]

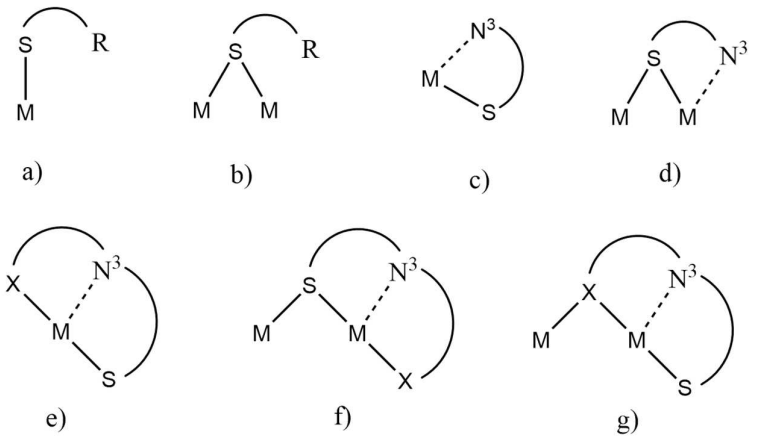


Figure 4. Binding of neutral thiosemicarbazone ligand: a) and b) monodentate, c) and d) bidentate and e) f) and g) tridentate.

In an anionic form, ligands can achieve the same monodentate, bidentate and tridentate binding modes as in the neutral form (Figure 4) with three additional possibilities shown in Figure 5: a) N^2S chelation, b) N^2S with bridging sulphur atom and c) rare example of pentacoordinated ligand.

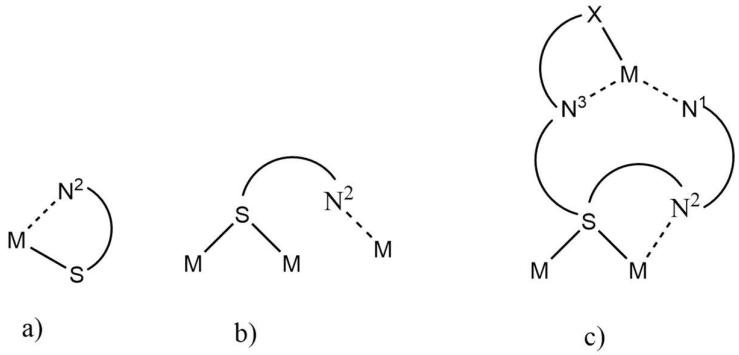


Figure 5. Binding of anionic thiosemicarbazone ligand.

Salicylaldehyde thiosemicarbazone (H_2SalTSC or H_2L) is the most studied ligand providing tridentate *ONS* coordination.[10] It usually coordinates the metal centre through the phenolic-oxygen, imine-nitrogen N^3 atom and thione/thiol-sulphur atom as monoanionic (HL^-, after deprotonation of –OH group) or dianionic ligand (L^{2-}, after deprotonation of –OH and $-N^2H$ groups). Figure 6 shows ligand coordination to the metal centre in its thione (a) or thiol (b) form. Rare coordination modes of this ligand are shown in Figure 6c and 6d. Coordination mode presented in Figure 6c is a rare example of ruthenium and osmium

complexes with the bidentate *NS* donor ligand forming a four-membered chelate ring.[11] The structure shown in Figure 6d is an example of the Mo(VI) complex in which salicylaldehyde thiosemicarbazone is coordinated as tridentate *ONN* ligand with deprotonated amide nitrogen N^1 instead of the thiocarbonyl sulphur atom.[10]

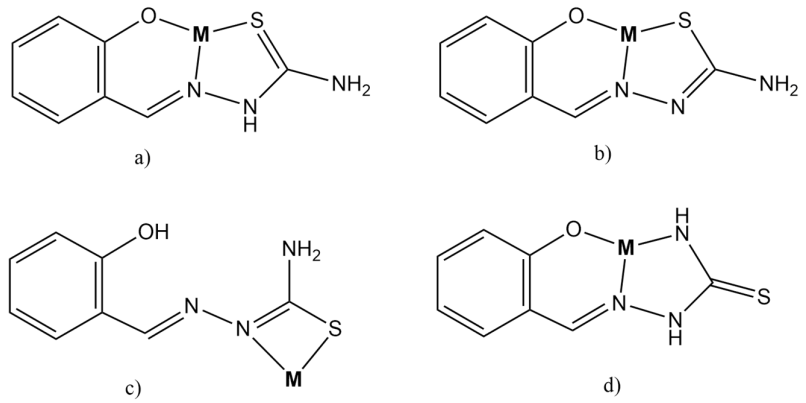


Figure 6. Coordination modes of salicylaldehyde thiosemicarbazone: a) *ONS* monoanionic, b) *ONS* dianionic c) *NS* bidentate and d) *ONN* tridentate.

2.2. Molybdenum(VI) complexes with *ONS* donor ligands

Nowadays, considerable interest is devoted to the chemistry of molybdenum complexes, especially with ligands that mimic the coordination environment of molybdoenzymes.[2] Consequently, a number of molybdenum complexes with tridentate Schiff bases have been synthesized and studied.[3,4] Since this thesis research was based on the Mo(VI) complexes with *ONS* ligands, the most relevant ones will be presented herein.

Generally, dioxo molybdenum(VI) complexes with *ONS* type of thiosemicarbazone ligand can be divided into three groups, Figure 7. Mononuclear complexes $[MoO_2(L)(D)]$, where D is donor molecule and L^{2-} corresponding ligand, dinuclear $[MoO_2(L)]_2$ and polynuclear ones $[MoO_2(L)]_n$. They are usually prepared by the reaction of $[MoO_2(acac)_2]$ or $[MoO_2Cl_2]$ with thiosemicarbazone ligand in methanol, acetonitrile or dichloromethane. Therefore, such complexes consist of *cis*-$\{MoO_2\}^{2+}$ core and a tridentate *ONS* donor ligand coordinated through the phenolic-oxygen, imine-nitrogen and thione/thiol-sulphur atom. Coordination is distorted octahedral, with sixth coordination site occupied by the donor molecule (D) in case of mononuclear or by the oxygen atom from Mo=O unit of the neighbouring molecule in case of dinuclear and polynuclear complexes (Figure 7).

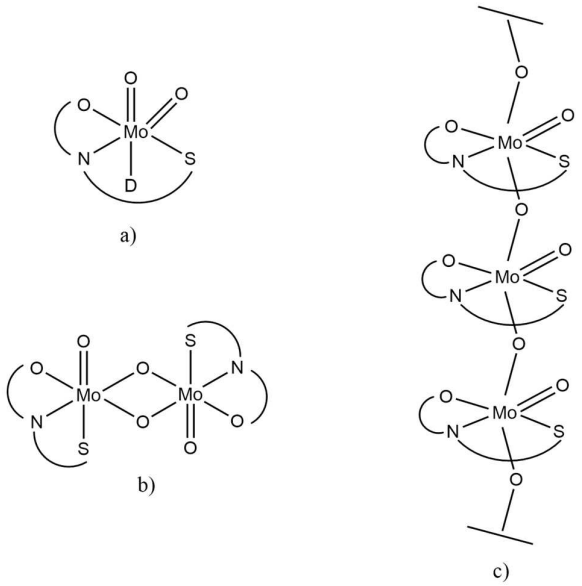
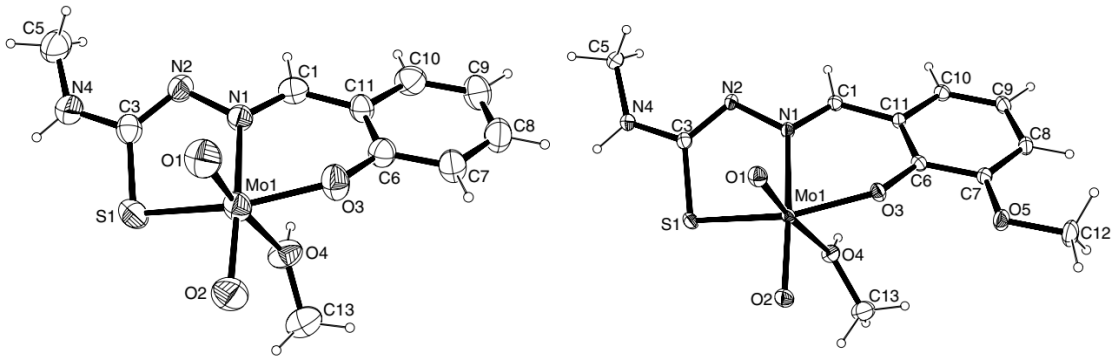


Figure 7. Usual types of dioxo molybdenum(VI) complexes with *ONS* donor ligand: a) mononuclear, d) dinuclear and c) polynuclear.

Two molecular structures of molybdenum(VI) complexes coordinated by salicylaldehyde 4-methylthiosemicarbazone (SalTSC-4-Me) (Figure 8a) and by 3-methoxysalicylaldehyde 4-methylthiosemicarbazone ligand (VanTSC-4-Me) (Figure 8b) were obtained from the methanolic solution of the corresponding polynuclear complex $[MoO_2(L)]_n$.[12] Both complexes are additionally coordinated by methanol molecule.



a) $[MoO_2(SalTSC\text{-}4\text{-}Me)(MeOH)]$ b) $[MoO_2(VanTSC\text{-}4\text{-}Me)(MeOH)]$

Figure 8. Structure of mononuclear molybdenum(VI) complexes: a) $[MoO_2(SalTSC\text{-}4\text{-}Me)(MeOH)]$ and b) $[MoO_2(VanTSC\text{-}4\text{-}Me)(MeOH)]$.[13]

Methanol molecule can be easily replaced by the neutral monodentate Lewis bases (*e.g.* pyridine, γ-picoline, imidazole *etc.*). For instance, $[MoO_2(SalTSC)(MeOH)]$ complex undergoes a methanol substitution with Lewis base (D) as shown in equation 1.[13,14]

$$[MoO_2(SalTSC)(CH_3OH)] + D \rightarrow [MoO_2(SalTSC)(D)] + CH_3OH \qquad (1)$$

Oligomerization and polymerization of mononuclear complexes are very favourable in weak donor solvents. This was established for the $[MoO_2(SalTSC)]_2$ and $[MoO_2(SalTSC)]_n$ complexes, respectively, obtained from dichloromethane or acetonitrile solution. Conversely, upon heating these complexes in methanol, the initial mononuclear complex was formed.[13]

Although the generation of polynuclear complexes in acetonitrile solution is more favoured, Moradi-Shoeili and coworkers[15] isolated brown crystals of the mononuclear complex $[MoO_2(L)(CH_3CN)]$ (Figure 9), in which ligand was derived from the 4-hydroxysalicylaldehyde and 4-methyl-4-phenylthiosemicarbazide.

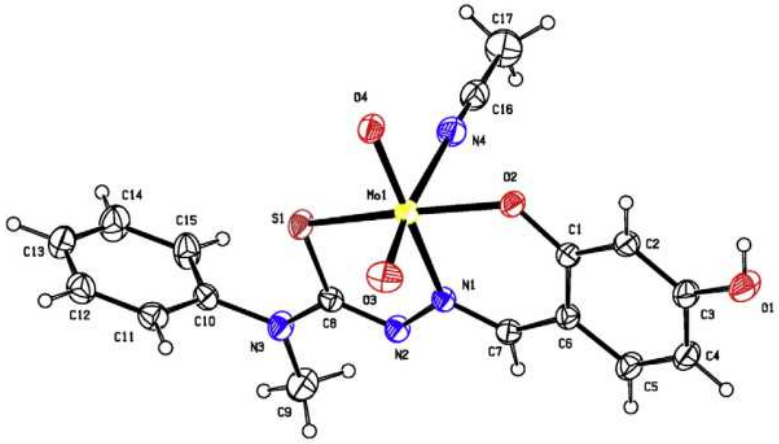


Figure 9. Structure of the $[MoO_2(L)(CH_3CN)]$ (L=4-hydroxysalicylaldehyde 4-methyl-4-phenylthiosemicarbazone).

Dinuclear Mo(VI) complex with salicylaldehyde thiosemicarbazone ligand was obtained by warming up the mixture of $[MoO_2(acac)_2]$ and salicylaldehyde thiosemicarbazone in dry dichloromethane. Also, warming the solution of $[MoO_2(SalTSC)CH_3OH)]$ in dichloromethane gave the same product. Structure of this complex is shown in Figure 10 and it contains two mononuclear units connected with a double oxygen bridge.

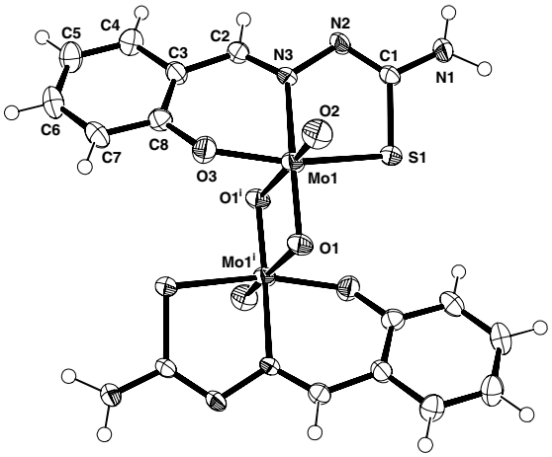


Figure 10. Structure of dinuclear $[MoO_2(SalTSC)]_2$.[13]

Unlike dinuclear, polynuclear complexes exhibit a linear chain with bridging through the terminal oxygen atoms (Mo=O···Mo=O···). Additionally, in the case of pyridoxal 4-phenylthiosemicarbazone ligand, bridging can be accomplished by the coordination of the hydroxymethyl oxygen from the neighbouring complex molecule.[16] These two types of coordination are shown in Figure 11 for the Mo(VI) complexes with pyridoxal thiosemicarbazone ligands.

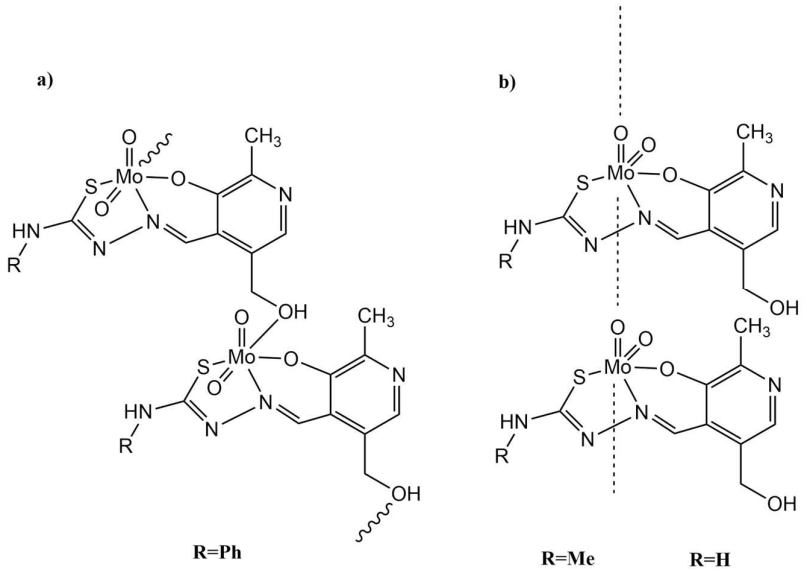


Figure 11. Structures of Mo(VI) complexes with a) pyridoxal 4-phenylthiosemicarbazone ligand (R=Ph) and coordination through the hydroxymethyl oxygen atom and b) pyridoxal 4-methylthiosemicarbazone ligand (R=Me) or pyridoxal thiosemicarbazone ligand (R=H) with coordination through oxo-ligand.

Polynuclear complex with pyridoxal 4-phenylthiosemicarbazone (Figure 11a) can be converted into corresponding mononuclear one upon dissolution in methanol. The opposite transformation will also occur upon heating the mononuclear complex in acetonitrile solution.

IR spectra of mononuclear complexes show two characteristic absorption bands in the range of 890-940 cm^{-1} corresponding to the Mo=O bonds of *cis*-$\{MoO_2\}^{2+}$ moiety. On the other hand, dinuclear and polynuclear complexes usually show one Mo=O vibrational band within the 910-950 cm^{-1}, and very intensive one within 800-850 cm^{-1} due to the Mo=O···Mo=O interaction.[17]

2.3. Polyoxomolybdates

Polyoxometalates (POMs) are anionic structures containing metal-centred MO_n polyhedra. They usually involve atoms of V, Nb, Ta, Cr, Mo or W, but the most numbered ones are with Mo, V or W atoms.[14] Polyoxomolybdates with molybdenum atoms octahedrally coordinated by six oxygen atoms are well studied. The most researched one is hexamolybdate anion $\{Mo_6O_{19}\}^{2-}$ (Lindqvist type), Figure 12. The most common preparation method involves synthesis in aqueous or non-aqueous solutions, either by a bench-top method or by hydrothermal synthesis.[19]

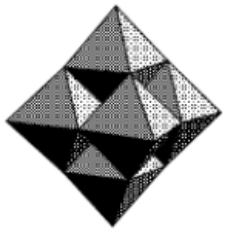


Figure 12. Coordination polyhedral of Lindqvist type of hexamolybdate $\{Mo_6O_{19}\}^{2-}$.[18]

In hybrid organic-inorganic POMs, metal complex cations are providing a charge compensation for polyoxometalate anion. In "so-called" functionalized POMs, metal complexes are covalently linked to the polyoxometalate anion. Recently both types of hybrids based on Lindqvist $\{Mo_6O_{19}\}^{2-}$ anion and Schiff base *ONO* donor ligand (Figure 13) were isolated.[20,21] The hybrid compounds were obtained from the wet acetonitrile solution in the reaction with $[MoO_2(acac)_2]$ and ligand, in 7:1 ratio. Additionally, it was confirmed that wet acetonitrile is important for the acetylacetonate complex hydrolysis and formation of the Lindqvist anion.[20]

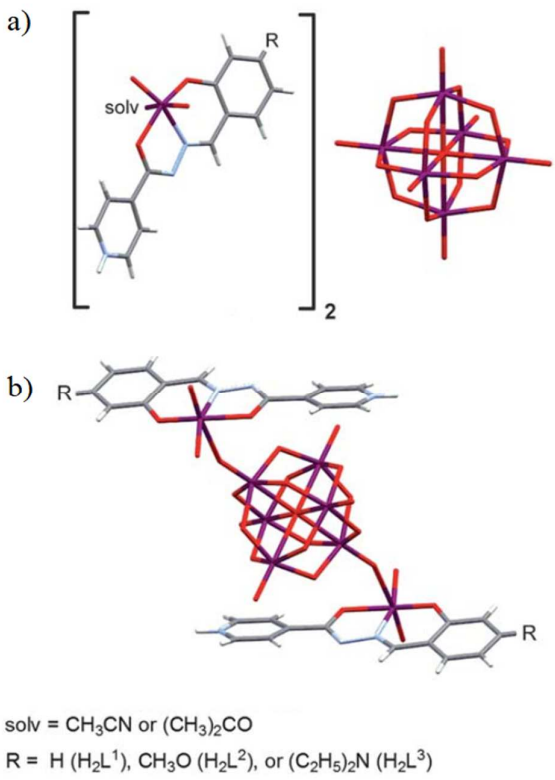


Figure 13. Structures of hybrid organic-inorganic compounds with the Lindqvist polyoxomolybdate and various cation/solvent combinations. In a) six coordination site of the complex cation is occupied by the solvent molecule whereas in b) Lindqvist anion is coordinated to the Mo(VI) core trough terminal oxo groups.[21]

2.4. Solvent-free epoxidation of olefins catalyzed by molybdenum complexes

2.4.1. Introduction to the green chemistry and catalysis

Nowadays, there is a great necessity for developing environmentally friendlier and more sustainable chemical processes, following the 12 Principles of Green Chemistry.[22] Those principles are the best ones to tend to eliminate organic solvents thus minimizing amounts of waste. Green catalytic alternatives are probably the most needed for the oxidation reactions that include conversion of oil- and natural gas-based feedstock to industrial organic chemicals. This includes olefin epoxidations that will be described in the next section.[22]

Majority of catalyses are homogeneous which means that reactants, products and catalyst are present in the same phase. Therefore, catalysts are usually soluble metal salts or

complexes. On the other hand, in heterogeneous catalytic reactions, substrate and catalyst are in different phases. Such a system usually involves solid catalyst and gas or liquid reactants.[18] If we consider a reaction where a reactant (R) gives a product (P) and by-products (Q) using a catalyst (cat), the reaction could be schemed as followed:

$$R \xrightarrow{cat} P + Q$$

Important parameters that describe catalytic efficient processes are conversion (CON_R), selectivity (S), turnover number (TON) and turnover frequency (TOF).

The conversion of a reactant R (CON_R) expresses the percentage of reactant consumed. It is mathematically defined as the ratio between the amount of transformed reactant R (at a considered reaction time t_x) and the initial amount that was introduced into the reactor $n_{R(0)}$ (at t=0) (equation 2). Since the direct information obtained is the present species at any time $n_{R(t)}$ and not the consumed ones, the equation has been defined according to it.

$$\mathrm{CON_R} = \frac{n_{R\ consumed}}{n_{R(0)}} \times 100\ (\%) = \frac{n_{R(0)} - n_{R(t)}}{n_{R(0)}} \times 100\ (\%) \qquad (2)$$

The selectivity (S_P) gives information about the efficiency of the reaction towards a studied product P. It is mathematically expressed as the molar ratio (in percentage) at a time *t* between the desired product P formed $n_{P(t)}$ and the reactant R consumed $n_{R\ consumed}$. Since the direct information obtained is the present species at any time $n_{(R,t)}$ and not the consumed ones, the equation has been defined according to it (equation 3).

$$S_P = \frac{n_{P(t)}}{n_{R\ consumed}} \times 100\ (\%) = \frac{n_{P(t)}}{n_{R(0)} - n_{R(t)}} \times 100\ (\%) \qquad (3)$$

TON (Turn Over Number) specifies the number of catalytic cycles that a catalyst can do, *i.e.* the number of molecules of reactant R that can be converted with one molecule of the catalyst. It is mathematically expressed as the amount of product P produced up to the time *t* and amount of catalyst. This value is normally calculated at the end of a reaction and shows the higher number of cycles (equation 4).

$$\text{TON} = \frac{n_{R\ consumed}}{n_{catalyst}} = \frac{n_{R(0)} - n_{R(t)}}{n_{catalyst}} \quad (4)$$

TOF (Turn Over Frequency) defines the activity of a catalyst according to time intervals. It is mathematically defined as the ratio between the number of moles of R transformed in a time interval Δt (between t_x and t_{x+1}) and the number of moles of catalyst divided by the time interval. It shows the activity of a catalytic centre (highest slope in the kinetic profile) *i.e.* the number of molecules of reactant consumed per time unit (equation 5).[18,23]

$$\text{TOF} = \frac{n_{R\ consumed\ in\ \Delta t}}{n_{catalyst}} \times \frac{1}{\Delta t} = \frac{n_{R(t_x)} - n_{R(t_{x+1})}}{n_{catalyst}} \times \frac{1}{t_{x+1} - t_x}\ (time^{-1}) \quad (5)$$

Also, another useful parameter is a mass balance which is used for the evaluation of the monitoring data (R, P, Q) in the reaction. In the catalysis, it is mathematically described as a ratio between the number of moles of R, P and Q in time *t* and the number of moles of R at the beginning of the reaction (equation 6).

$$\text{Mass balance} = \frac{n_{R(t)} + n_{P(t)} + n_{Q(t)}}{n_{R\ (0)}} \times 100\ (\%) \quad (6)$$

2.4.2. Solvent-free epoxidation

Catalytic epoxidation of olefins is of interest since epoxides are important intermediates and precursors to many pharmaceuticals and fine chemicals.[24] In conventional organic synthesis, they can be obtained using strong organic oxidants and solvents, but with low selectivity due to the ring opening process of the epoxide. On the other hand, solvent-free epoxidation of olefins involves oxidation with hydrogen peroxide or alkyl hydroperoxide catalysed by transition metal complexes in the absence of organic solvents.[5-7,25,26]

Tert-butyl hydroperoxide (TBHP) is more often used than H_2O_2 because of its solubility and stability in organic solvents. Also, the overall oxidation process is cheaper since *tert*-butanol (*t*BuOH), the by-product of the reaction, can be recycled or converted into gasoline additive methyl *tert*-butyl ether (MTBE). Further, aqueous H_2O_2 has a lower concentration of oxidant (30 % in case of H_2O_2 and 70 % in case of TBHP) and during the reaction produces additional water which may lead to the faster ring opening and therefore lower selectivity.[25]

2.4.3. Molybdenum(VI) complexes as catalyst

Among all metals used in catalysis, Mo(VI) complexes have shown the best activity in epoxidation reactions with alkyl hydroperoxides as oxidants.[27] They are widely used in academic research and industry. For example, propylene oxide is currently manufactured on a large scale by molybdenum-catalysed epoxidation of propylene with aqueous TBHP (Figure 14).[27]

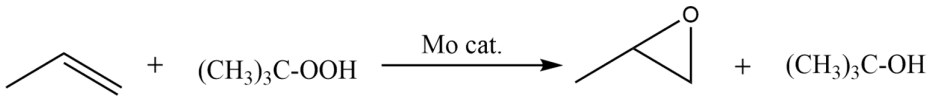


Figure 14. Solvent-free epoxidation of propylene.

The most used catalysts are dioxomolybdenum(VI) complexes because of the high reaction yield, facile preparation and its stability. Various Mo(VI) complexes with tridentate *ONO* and *ONS* Schiff base ligands have been tested in organic solvents and proven to be efficient catalysts.[28-30] In order to develop a cleaner process, some complexes started to be examined under organic solvent-free conditions. For example, mononuclear and polynuclear pyridoxal hydrazonato and especially pyridoxal thiosemicarbazonato molybdenum(VI) complexes showed high activity and selectivity with a just 0.05 % of catalyst *vs.* substrate loading.[6,7,18] Furthermore, hybrid organic-inorganic compounds with dioxomolybdenum complex cation and Lindqvist anion were also tested as (pre)catalysts for epoxidation of olefins under solvent-free conditions.[18] However, complexes with *ONS* pyridoxal thiosemicarbazonato ligands obtained better results, especially in a mononuclear form, which was observed to be the best one reported at that time (highest TOF and TON values).

Figure 15 shows a general mechanism for olefin epoxidation that was proposed.[26,28] Mo(VI) complexes with tridentate Schiff base ligand can generate 5-coordinated [MoO_2L] intermediate by dissociation of a weakly coordinated alcohol or by dimer splitting. A neutral molecule of TBHP oxidant than occupies sixth coordination site, assisted with the HO···H hydrogen bond, thus forming a [MoO_2(L)(*t*-BuOOH)] complex. The metal centre withdraws electrons from the O–O bond of coordinated peroxide which makes it more approachable for nucleophilic olefin attack.[22]

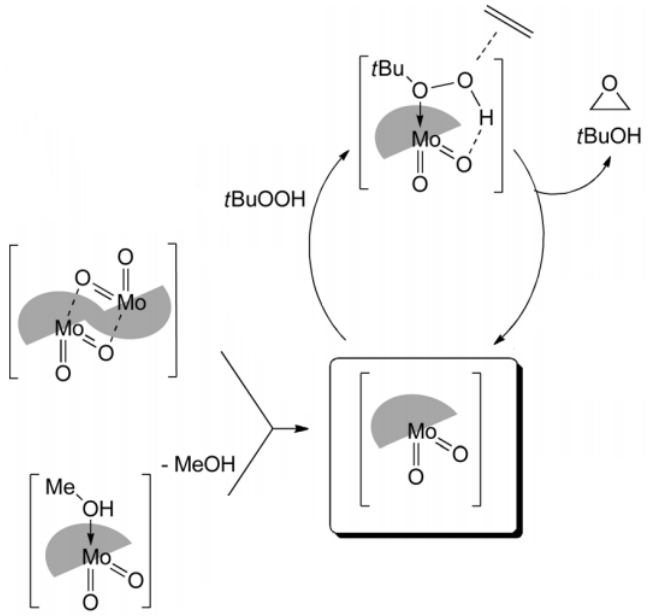


Figure 15. Proposed mechanism for the catalytic epoxidation of olefins by dioxomolybdenum(VI) complexes and TBHP as oxidant.[26]

2.4.4. Selected epoxidation substrates

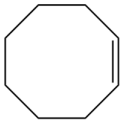
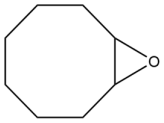
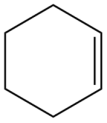
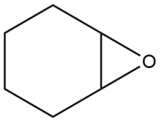
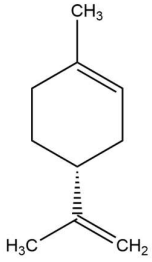
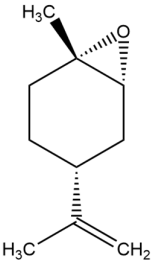
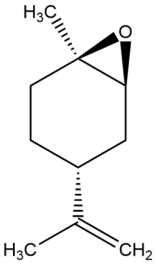
In this thesis solvent-free epoxidation was examined on three substrates: *cis*-cyclooctene, cyclohexene and (*R*)-limonene, Table 1.

Cyclooctene (CO) is a commonly used model substrate for testing a new catalyst. Compared to the other cycloalkenes, his major oxidation product is the corresponding epoxide, usually with high selectivity.

Cyclohexene (CH) can be oxidised into cyclohexene oxide (CHO) which is used in the synthesis of several products such as chiral pharmaceuticals, epoxy paints, pesticides and dyestuffs. However, in an aqueous media, selectivity towards epoxide is often low due to the ring opening process of cyclohexene oxide and transformation into cyclohexene diol (CHD).

Limonene (Lim) is a monoterpenic compound and suitable catalyst model for terpene epoxidation. As the main component of citrus oil, limonene is commercially obtained from the fruit juice industry as a waste product. Even so, this waste product can be oxidised into limonene oxide which is a very important material for the industry of food, perfumes and cosmetics. In Table 1 are shown structures of olefin substrates, desired products and their potential applications.

Table 1. List of epoxidation substrates, desired products and use of desired products.

SUBSTRATE	DESIRED PRODUCT		USE OF DESIRED PRODUCT
 cyclooctene	 cyclooctene oxide		-modal substrate for cyclooctene epoxidation
 cyclohexene	 cyclohexene oxide		-chiral pharmaceuticals -pesticides -epoxy paints -rubber promoters -dyestuffs
 (*R*)-limonene	 *trans*-limonene	 *cis*-limonene	-modal substrate for terpene epoxidation, -fragrances -perfumes -food additives -pharmaceuticals

§ 3. EXPERIMENTAL SECTION

Solvents and starting reagents were commercially available and used without previous purification.

Infrared spectra were recorded with a Perkin–Elmer 502 spectrophotometer in the region of 4400–450 cm^{-1}, using Attenuated Total Reflectance technique (ATR).

Thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA851 thermobalance using aluminium crucibles, under the oxygen atmosphere and within the temperature range from 25 to 600 ˚C with a heating rate of 10 ˚C min^{-1}.

Molecular and crystal structures of mononuclear complexes were determined by the single-crystal X-ray diffraction at the Division of General and Inorganic Chemistry.

Chromatograms were obtained using Agilent 7820A chromatograph with FID detector and HP5-MS capillary column (30 m x 0.32 mm x 0.25 μm). The GC parameters were quantified with authentic samples of the reactants and products. Conversion of olefins and formation of corresponding epoxides and diols were calculated from calibration curves (R^2 = 0.999) relative to acetophenone as an internal standard.

3.1. Preparation of the starting compounds

3.1.1. Dioxobis(2,4-pentanedionato)molybdenum(VI), [$MoO_2(acac)_2$]

4 mL (2,4 mmol) of acetylacetone $C_5H_8O_2$ was added to the aqueous solution of ammonium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 3 g (0,04 mmol) in 10 mL. A pH value of the solution was carefully adjusted to 3.5 with addition of HNO_3 (*w*=10 %) and stirred for one hour. After two hours the yellow precipitate was filtered off and rinsed with water and ethanol. Yield: 1.67 g (30.1 %).

3.1.2. $H_2$5MeO-SalTSC-4-Ph thiosemicarbazone

0.82 g (4.9 mmol) of 4-phenyl-3-thiosemicarbazide was dissolved in 40 mL of methanol and a methanolic solution of 5-methoxy-2-hydroxybenzaldehyde, 0.76 g (5.0 mmol) in 10 mL, was slowly added and stirred. The resulting yellow solution was refluxed and stirred for two more hours. After five days the obtained white product was filtered off. Yield: 0.77 g (52.2 %).

3.1.3. $H_2$5MeO-SalTSC-4-Me thiosemicarbazone

0.52 g (4.9 mmol) of 4-methyl-3-thiosemicarbazide was dissolved in 25 mL of methanol and a methanolic solution of 5-methoxy-2-hydroxybenzaldehyde, 0.76 g (5.0 mmol) in 10 mL, was slowly added and stirred. The resulting yellow solution was refluxed and stirred for two more hours and the yellow precipitate was observed. After five days the bright yellow product was filtered off. Yield: 0.98 g (82.6 %).

3.1.4. $H_2$5MeO-SalTSC thiosemicarbazone

0.45 g (4.9 mmol) of thiosemicarbazide was dissolved in 20 mL of methanol and a methanolic solution of 5-methoxy-2-hydroxybenzaldehyde, 0.76 g (5.0 mmol) in 10 mL, was slowly added and stirred. The resulting yellow solution with white precipitate was refluxed and stirred for two more hours and after five days the bright yellow product was filtered off. Yield: 0.86 g (77.2 %).

3.2. Synthesis of molybdenum(VI) complexes

3.2.1. $[MoO_2$(5MeO-SalTSC-4-Ph)$]_n$

0.092 g (3.065×10^{-4} mol) of the $H_2$5MeO-SalTSC-4-Ph ligand was dissolved in 20 mL of acetonitrile and 0.1 g (3.065×10^{-4} mol) of $[MoO_2(acac)_2]$ was added. The orange reaction mixture was refluxed for 3 hours at 50-60 ˚C. The mixture was left at room temperature for five days and the brown product was filtered off. Yield: 0.13 g (98.6 %).

3.2.2. $[MoO_2$(5MeO-SalTSC-4-Me$)]_n$

0.073 g (3.065×10^{-4} mol) of the $H_2$5MeO-SalTSC-4-Me ligand was dissolved in 20 mL of acetonitrile and 0.1 g (3.065×10^{-4} mol) of $[MoO_2(acac)_2]$ was added. The orange reaction mixture was refluxed for 3 hours at 50-60 ˚C. The mixture was left at room temperature for five days and the brown product was filtered off. Yield: 0.09 g (77.5 %).

3.2.3. $[\{MoO_2$(5-MeO-SalTSC$)\}\cdot\frac{1}{2}CH_3CN]_n$

0.069 g (3.065×10^{-4} mol) of the $H_2$5MeO-SalTSC ligand was dissolved in 20 mL of acetonitrile and 0.1 g (3.065×10^{-4} mol) of $[MoO_2(acac)_2]$ was added. The yellow reaction mixture was refluxed for 3 hours at 50-60 ˚C. After prolonged standing at room temperature, the crystals lose crystallized acetonitrile molecule and were analysed as [MoO_2(5MeO-

SalTSC)]$_n$. The mixture was left at room temperature for five days and the black product was filtered off. Yield: 0.10 g (88.3 %).

3.2.4. [MoO_2(5MeO-SalTSC-4-Me)(MeOH)]

0.073 g (3.065×10^{-4} mol) of the $H_2$5MeO-SalTSC-4-Me ligand was dissolved in 20 mL of methanol and 0.1 g (3.065×10^{-4} mol) of [$MoO_2(acac)_2$] was added. The orange reaction mixture was refluxed for 3 hours at 50-60 ˚C and left at room temperature for five days. The obtained dark red crystals were filtered off. Yield: 0.11 g (89.0 %).

3.2.5. [MoO_2(5MeO-SalTSC)(MeOH)]·MeOH

0.069 g (3.065×10^{-4} mol) of the $H_2$5MeO-SalTSC ligand was dissolved in 20 mL of methanol and 0.1 g (3.065×10^{-4} mol) of [$MoO_2(acac)_2$] was added. The orange reaction mixture was refluxed for 3 hours at 50-60 ˚C and left at room temperature for five days. The obtained dark red crystals were filtered off. After prolonged standing at room temperature, the crystals lose crystallized methanol molecule and were analysed as [MoO_2(5MeO-SalTSC)(MeOH)]. Yield: 0.08 g (67.5 %).

3.2.6. [MoO_2(H5MeO-SalTSC-4-Me)(CH_3CN)]$_2Mo_6O_{19}$

0.020 g (0.085 mmol) of the $H_2$5MeO-SalTSC-4-Me ligand was dissolved in 80 mL of acetonitrile and 0.196 g (0.6 mmol) of [$MoO_2(acac)_2$] was added. The orange reaction mixture was gently heated for 4 hours and left at room temperature. Next day the reaction mixture with the yellow precipitate was filtered and the solution was covered with drilled parafilm. After five days solvent was evaporated up to 10-15 mL and the orange precipitate started to deposit. After two days the product was filtered off. Yield: 0.14 g (29.7 %).

3.3. General procedure for the epoxidation of olefins by aqueous TBHP

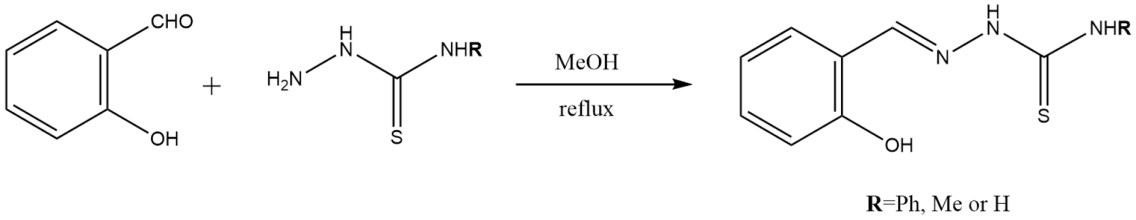
Procedure A: 20 mmol of appropriate olefin (2.76 mL of *cis*-cyclooctene or 2.03 of cyclohexene or 3.4 mL of *R*-limonene) and 6-7 drops of acetophenone were stirred together. 0.05 % of Mo(VI) (pre)catalyst was added in the mixture *i.e.* 0.01 mmol of the polynuclear and mononuclear complex or 0.005 mmol of the polyoxomolybdate. The mixture was stirred and heated up to 80 ˚C before adding 40 mmol of aqueous TBHP oxidant (70 wt %, 5.48 mL). *Procedure B*: 1 μL of methanol (0.025 mmol) was added to the mixture of cyclooctene, acetophenone and catalyst. The mixture was heated 10 minutes up to 80 ˚C and the oxidant was added.

All the reactions were monitored for 6 h. At defined times 0, 20, 50, 90, 150, 270 and 360 minutes, aliquots (≈0.1 mL) of the organic phase were taken from the reaction media and mixed with Et_2O. Catalytic reactions were followed along the time through the GC measurements.

§ 4. RESULTS AND DISCUSSION

4.1. Thiosemicarbazone ligands

The thiosemicarbazone ligands were prepared by the condensation reaction of 5-methoxy-2-hydroxybenzaldehyde and corresponding thiosemicarbazide in the refluxing methanolic solution (Scheme 1). All ligands were obtained in high yield.



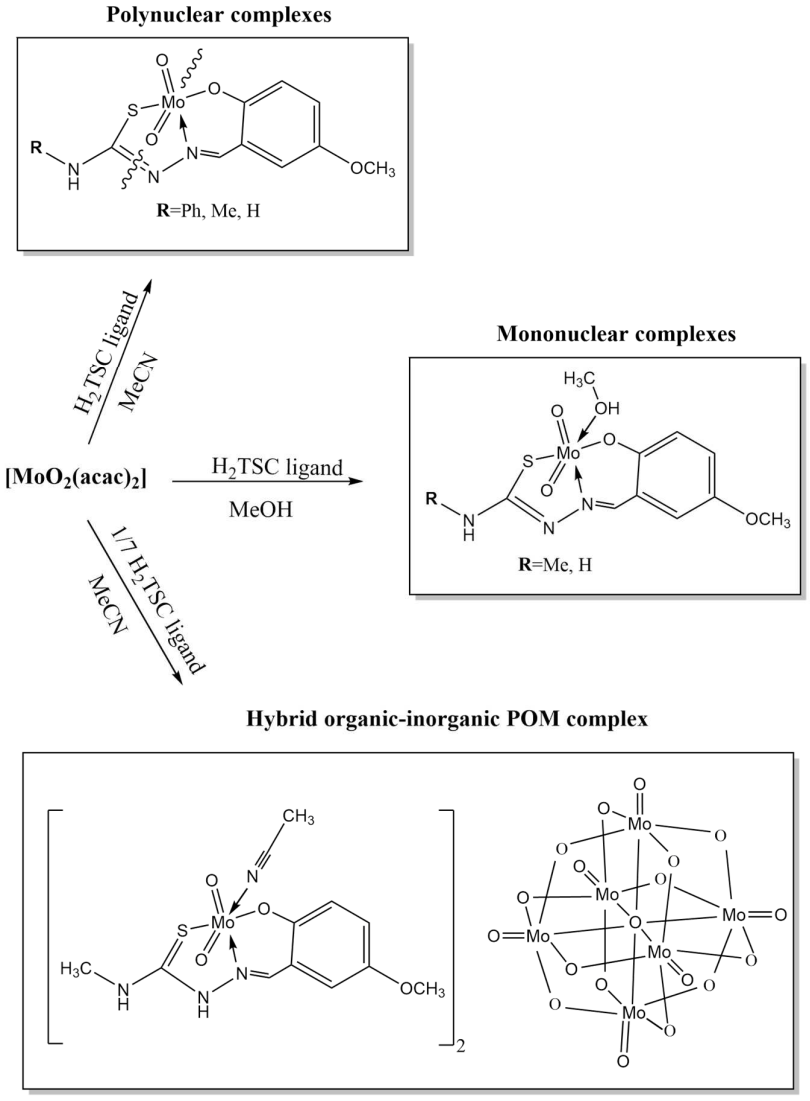
R=Ph, Me or H

Scheme 1. Synthesis of thiosemicarbazone ligands.

4.2. Dioxomolybdenum(VI) complexes: synthesis and characterization

Mononuclear and polynuclear molybdenum complexes were obtained by the reaction of the corresponding thiosemicarbazone ligand and $[MoO_2(acac)_2]$ complex (1:1 molar ratio) in methanol or acetonitrile solution at 50-60 °C. From methanolic solution, dark red crystals of the mononuclear complexes $[MoO_2$(5MeO-SalTSC-4-Me)(MeOH)] and $[MoO_2$(5MeO-SalTSC)(MeOH)]·MeOH were isolated whereas reaction in acetonitrile solution lead to the brown polynuclear products $[MoO_2$(5MeO-SalTSC-4-Ph)]$_n$ and $[MoO_2$(5MeO-SalTSC-4-Me)]$_n$ and black polynuclear product $[\{MoO_2$(5-MeO-SalTSC)$\}\cdot$½$CH_3CN]_n$ (Scheme 2). However, the mononuclear complex $[MoO_2$(H5MeO-SalTSC-4-Ph)(MeOH)] could not be isolated because of its tendency to polymerise. The complexes $[MoO_2$(5MeO-SalTSC)(MeOH)]·(MeOH) and $[\{MoO_2$(5-MeO-SalTSC)$\}\cdot$½$CH_3CN]_n$ lose additional solvent molecule by standing at room temperature and were analysed as $[MoO_2$(5MeO-SalTSC)(MeOH)] and $[MoO_2$(5-MeO-SalTSC)]$_n$. The reaction of $[MoO_2(acac)_2]$ complex and H$_2$5MeO-SalTSC ligand in acetonitrile solution and 7:1 molar ratio provided the orange hybrid organic-inorganic polyoxomolybdate complex $[MoO_2$(H5MeO-SalTSC-4-Me)$(CH_3CN)]_2Mo_6O_{19}$ (Scheme 2). As mentioned earlier, it was proven that wet acetonitrile is important for the hydrolysis of the acetylacetonate complex and the formation of the

Lindvist anion. In this case, the reaction mixture was left covered with drilled parafilm for five days allowing the air moisture to participate in the formation of the Lindqvist anion.



Scheme 2. Presentation of the polynuclear and mononuclear molybdenum(VI) complexes and the hybrid organic-inorganic polyoxometalate with thiosemicarbazone ligands.

Molecular and crystal structures were determined for the mononuclear complexes $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$ (Figure 16) and $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]\cdot MeOH$ (Figure 17). In both structures, thiosemicarbazone ligand is coordinated in doubly-deprotonated L^{2-} form through the phenolic-oxygen, imine-nitrogen and thiol-sulphur atom. Also, the sixth coordination site of the central molybdenum atom is

occupied by the methanol molecule. In the case of [MoO_2(5MeO-SalTSC)(MeOH)]·MeOH complex, one additional methanol molecule was found in the crystal structure.

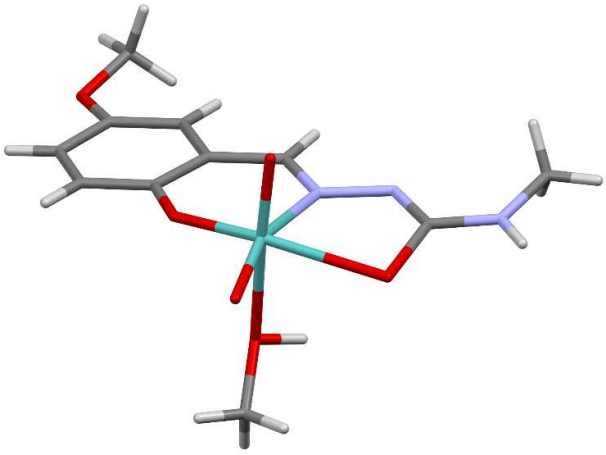


Figure 16. Molecular structure of [MoO_2(5MeO-SalTSC-4-Me)(MeOH)] complex.

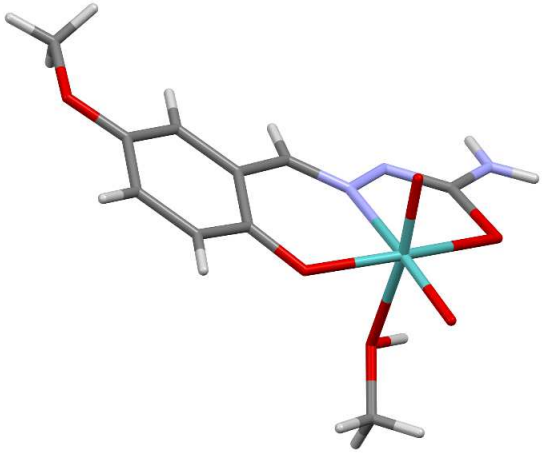


Figure 17. Molecular structure of [MoO_2(5MeO-SalTSC)(MeOH)]·MeOH complex. The crystallised methanol molecule is omitted for clarity.

In the IR spectra of polynuclear complexes the broad stretching bands belonging to *v*(OH) and *v*(N–H) (3412-3379 cm^{-1} and 3306-3138 cm^{-1}) that are present in the IR spectra of the free ligands disappear by complex formation. This indicates that the ligand is coordinated to the metal centre in doubly-deprotonated L^{2-} in thio-enol form. The stretching frequencies found at 1611-1602 cm^{-1} and 1552-1538 cm^{-1} region of the free thiosemicarbazones, attributed to C=N_{imine} and C–$O_{phenolic}$ bonds, are shifted to 1597-1591 cm^{-1} and 1570-1563 cm^{-1} region, respectively, in the corresponding complexes. This indicates the coordination

through the azomethine nitrogen and oxoaryl oxygen atom. The most important stretching bands for polynuclear complexes are intense broad bands around 794-788 cm^{-1} and single strong absorption band found in the 926-920 cm^{-1} region that were assigned to the Mo=O···Mo bridging and terminal MoO groups, respectively.

In the IR spectra of the mononuclear complexes, the stretching bands of ν(C=N) and ν(C–O) are shifted to 1628-1591 cm^{-1} and 1558-1555 cm^{-1}, respectively. Apart from the polynuclear complexes, the mononuclear ones show $\nu_{asym}(MoO_2)$ and $\nu_{sym}(MoO_2)$ stretching bands at 926-933 cm^{-1} and 895-887 cm^{-1}. ν(O–H) and ν(C–O) stretching vibrations of the coordinated methanol were found at 3428-3438 cm^{-1} and 1023-1009 cm^{-1}, respectively.

The IR spectra of the hybrid organic-inorganic complex with the Lindqvist anion $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$ shows strong absorption bands at 944 cm^{-1} and 784 cm^{-1} assigned to $Mo{=}O_t$ and $Mo{=}O_b$ stretching bonds of the hexamolybdate anion. $\nu_{asym}(MoO_2)$ stretching was found at 911 cm^{-1}, while $\nu_{sym}(MoO_2)$ one was overlapped by a strong band at 944 cm^{-1}. Absorption bands at 1619, 1551 and 3307 cm^{-1} correspond to the $\nu(C{=}N_{imine})$, $\nu(C{-}O_{phenolic})$ and ν(N–H) stretching, respectively. They point out the monoprotonated coordination of ligand in thio-keto form. The stretching band at 2273 cm^{-1} indicates coordination of the acetonitrile molecule to the sixth coordination site of the complex cation.

Selected stretching vibrations of molybdenum(VI) complexes are summarized in Table 2 and IR spectra of complexes and ligands are shown in the Supplement (Figure D1-9).

Table 2. Selected IR stretching vibrations of prepared molybdenum complexes.

	Selected IR data (cm^{-1})					
	MoO_2 (asym)	MoO_2 (sym)	Mo=O	Mo=O···Mo	C=N	C–O
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$			926	788	1591	1563
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$			920	794	1598	1570
$[\{MoO_2(5\text{-}MeO\text{-}SalTSC)\}\cdot ½CH_3CN]_n$			914	787	1597	1563
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$	926	895			1591	1555
$[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$	933	887			1589	1558
			$Mo{=}O_t$	$Mo{=}O_b$		
$[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$	911	944	944	784	1619	1551

The amount of C, H and N in complex compounds was determined by the elemental analysis. The results are shown in Table 3.

Table 3. Amount of C, H and N in prepared complex compounds.

	w_{exp} / % (w_{theor} / %)		
	C	H	N
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$	42.47 (42.16)	2.74 (3.07)	9.67 (9.83)
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$	32.63 (32.89)	2.54 (3.04)	11.28 (11.51)
$[MoO_2(5MeO\text{-}SalTSC)]_n$	30.90 (30.78)	2.89 (2.58)	11.65 (11.97)
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$	32.98 (33.25)	2.96 (3.81)	10.23 (10.58)
$[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$	31.09 (31.31)	3.12 (3.42)	11.76 (10.96)
$[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$	16.5 (17.01)	1.93 (1.78)	6.52 (6.61)

All molybdenum complexes were analysed by thermogravimetry, under the oxygen atmosphere and within the temperature range from 25 to 600 ˚C. Under these conditions, thermal decomposition resulted in the formation of molybdenum(VI) oxide MoO_3. Results are shown in Table 4.

Table 4. Results of thermogravimetric analysis.

	w_{exp} / % (w_{theor} / %)		
	Mo	MeOH	CH_3CN
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$	23.64 (22.46)		
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$	28.64 (26.27)		
$[\{MoO_2(5\text{-}MeO\text{-}SalTSC)\}\cdot ½CH_3CN]_n$	26.97 (25.81)		6.0 (5.52)
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$	25.81 (24.15)	6.3 (8.06)	
$[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$	25.85 (23.10)	7.4 (8.36)	
$[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$	45.92 (45.30)		4.4 (4.84)

The thermal analysis data of the polynuclear complexes $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$ and $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$ shows significant weight loss in the range of 253-584 ˚C and 241-545 ˚C corresponding to the complex decomposition (Supplement, Figure D10 and D11).

The polynuclear complex [{MoO_2(5-MeO-SalTSC)}·½CH_3CN]$_n$ decomposes in two steps (Supplement, Figure D12). In the first step (39-110 ˚C), complex loses 6 % of the mass which corresponds to the loss of crystallised acetonitrile molecule and conversion into stable [MoO_2(5Meo-SalTSC)]$_n$. However, the complex completely loses acetonitrile molecule by standing at room temperature and its presence can be established if it is analysed immediately after isolation which is the case in the IR spectroscopy and TG analysis but not in the elemental analysis. Upon further heating, the weight loss of 53.3 % in the range 233-479 ˚C indicates complex decomposition.

Thermogravimetric curves for the mononuclear complexes [MoO_2(5MeO-SalTSC-4-Me)(MeOH)] and [MoO_2(5MeO-SalTSC)(MeOH)] show decomposition in two step (Supplement, Figure D13 and D14). In the first step, weight loss of 6.3 % and 7.4 %, in the range of 57-168 ˚C and 65-203 ˚C, respectively, is attributed to the loss of coordinated methanol molecule and conversion into the corresponding polynuclear complex. In the second decomposition step (262-506 ˚C and 239-465 ˚C) complex decomposition occurs with a weight loss of 54 % and 26.7 %, respectively.

The thermal analysis data of the POM hybrid [MoO_2(H5MeO-SalTSC-4-Me)(CH_3CN)]$_2Mo_6O_{19}$ shows mass losses of 4.4 % and 26.7 % in the range of 65-203 ˚C corresponding to the loss of coordinated acetonitrile molecule and the POM complex decomposition, respectively (Supplement, Figure D15).

4.3. The catalytic activity of molybdenum complexes in the epoxidation of olefins

Prepared molybdenum complexes were tested in the catalytic epoxidation of *cis*-cyclooctene (CO), cyclohexene (CH) and *(R)*-limonene (Lim). The aim of this work was to determine the influence of: a) the substituent, b) type of the complex (polynuclear, mononuclear and POM hybrid) and c) methanol addition on polynuclear complexes.

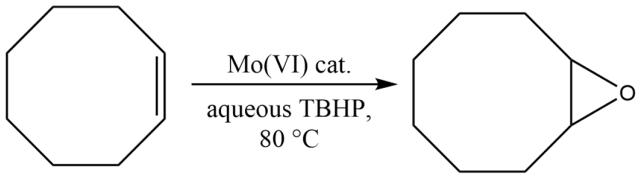
In order to follow the principles of green chemistry, olefins were oxidized with aqueous TBHP, without the addition of an organic solvent and with low catalyst loading (n(Mo in complex) : n(olefin) = 0.01 mmol : 20 mmol). All the complexes were insoluble or sparingly soluble in olefins at room temperature (orange-brown slurry) but dissolved completely in organic phase after addition of aqueous TBHP at 80 ˚C (orange mixture). The most insoluble complex was polynuclear [MoO_2(5MeO-SalTSC-4-Me)]$_n$, which dissolved within 30 minutes

after oxidant addition. In the reaction mixtures, two phases were observed: the aqueous colourless (or slightly coloured) and organic bright yellow phase. However, at the end of the epoxidation reactions of cyclohexene and limonene only one phase was present.

The conversion of substrates and the formation of products were calculated from the calibration curves relative to acetophenone (Supplement, Figure D16-25). Obtained results will be discussed in terms of conversion, selectivity and TON calculated after 6-hour reaction and TOF calculated after 20 min.

4.3.1. Epoxidation of cis-cyclooctene

Catalysed cyclooctene (CO) epoxidation reactions yielded cyclooctene oxide as the main product found in the organic phase. (Scheme 3).



Scheme 3. Cyclooctene epoxidation catalysed by molybdenum complexes.

The results of catalysis are compiled in Table 5. All the polynuclear and mononuclear catalysts show similar, high values of conversions (77-85 %). However, by using the POM hybrid catalyst conversion reaches up to 94 %. Selectivities are also high for all the complexes (around 90 %). Initial TOF values are very high considering low catalyst loading (0.05 %). The lowest one is for $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$ (1184 h^{-1}), and the highest one for $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$ complex (2641 h^{-1}).

Table 5. Results of the cyclooctene epoxidation catalysed with Mo(VI) complexes in the presence of aqueous TBHP at.

	Conv. CO / %	Selectivity (epoxide) / %	TOF_{20min} / h^{-1}	TON
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$	85	93	2641	1657
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$	82	85	1707	1320
$[MoO_2(5MeO\text{-}SalTSC)]_n$	78	93	1508	1540
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$	77	91	1184	1176
$[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$	82	88	1774	1645
$[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$	94	93	1508	3719
+ 1 μL MeOH				
$[MoO_2(5MeO\text{-}SalTSC\text{-}4Ph)]_n$	86	92	1800	1700
$[MoO_2(5MeO\text{-}SalTSC\text{-}4Me)]_n$	80	90	1308	1586
$[MoO_2(5MeO\text{-}SalTSC\text{-}TSC)]_n$	81	92	1513	1633

Concerning the ligand nature of polynuclear complexes, $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$ complex is the most active one and has the highest TOF value, possibly due to the faster and easier generation of the catalytically active pentacoordinated species (Figure 18). Nevertheless, selectivities for all the polynuclear complexes are very similar.

Comparing the kinetic profiles with polynuclear and mononuclear complexes (Figure 19) it was observed that the mononuclear complex $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$ is more active than the corresponding polynuclear one. The opposite effect was detected with a catalyst based on the $H_2$5MeO-SalTSC-4-Me ligand. Considering the type of complex used, the POM hybrid shows the best activity (Figure 18). The reason for such results could be the fact that Mo(VI) Lindqvist polyoxomolybdate complex, $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$, has two potential active sites, the $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)]^+$ cation and $Mo_6O_{19}^{2-}$ anion.[6]

Methanol addition to the reaction mixture with $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$ polynuclear catalyst slows down the reaction as a result of methanol coordination to the metal centre. At the end of the reaction conversion and selectivity are similar in both cases due to the presence of same active species in the solution. In the case of $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$ polynuclear complex, the addition of MeOH does not affect kinetic profile significantly, except at the very beginning where the slight slowdown is observed. On the other hand, a

slight increase of catalytic activity of $[MoO_2(5MeO\text{-}SalTSC)]_n$ polynuclear complex is observed. Reactions with methanol addition are shown in Supplement, Figure D26-28.

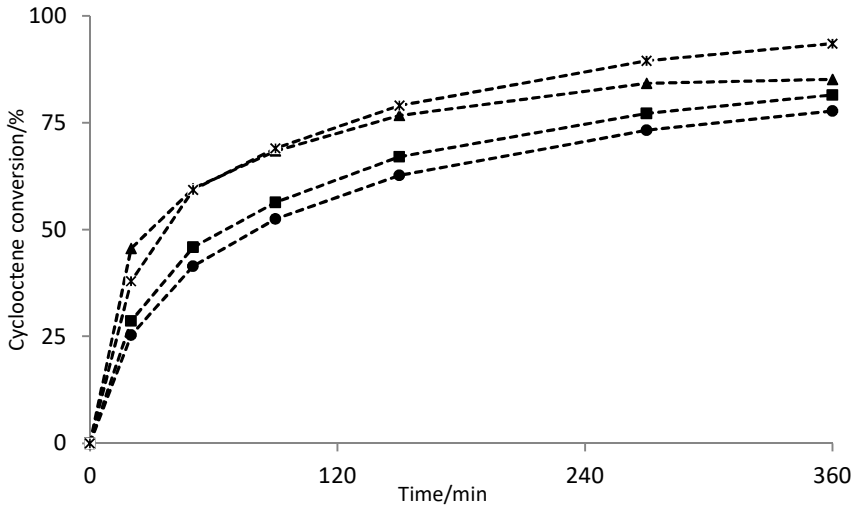


Figure 18. Converted cyclooctene *vs*. time with polynuclear dioxomolybdenum(VI) complexes and POM hybrid complex: ▲ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$, ■ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$, ● $[MoO_2(5MeO\text{-}SalTSC)]_n$ and ∗ $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.05/100/200, T = 353 K.

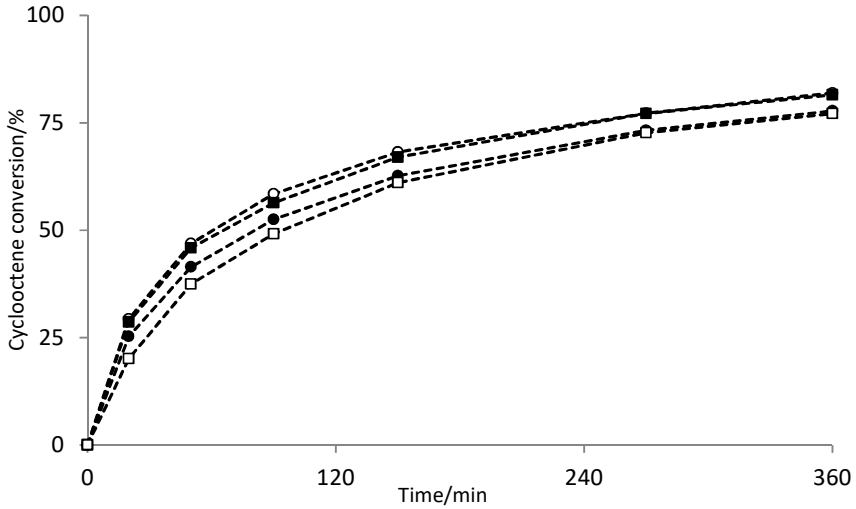


Figure 19. Converted cyclooctene *vs*. time with polynuclear and mononuclear dioxomolybdenum(VI) complexes: ■ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$, ● $[MoO_2(5MeO\text{-}SalTSC)]_n$, □ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$, ○ $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.05/100/200, T = 353 K.

Although cyclooctene epoxide is the main product, a slight decrease of mass balance is observed during the reactions due to the cyclooctene oxide transfer into water phase (Figure 20). That is also a reason for the negligible loss of selectivity in each reaction.

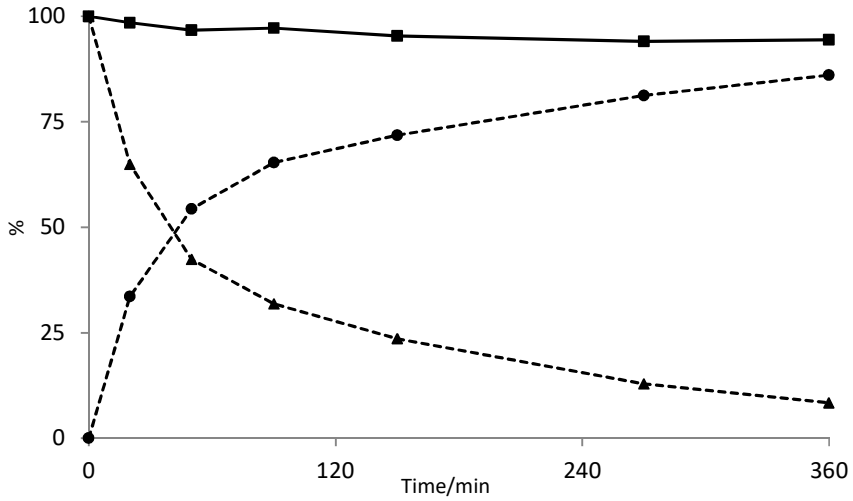
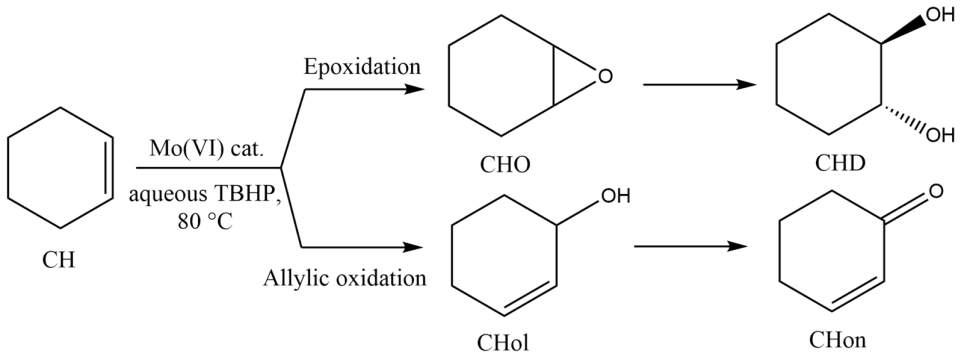


Figure 20. Conversion of cyclooctene (---▲---), formation of cyclooctene oxide (---●---) and mass balance (–■–) *vs*. time for POM hybrid catalyst, $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.05/100/200, T = 353K.

4.3.2. Epoxidation of cyclohexene

Cyclohexene oxidation reactions took place via two pathways (Scheme 4). In the main epoxidation reaction pathway, cyclohexene oxide (CHO) was formed and transformed into cyclohexane diol (CHD). Second allylic oxidation pathway yielded a small amount of 2-cyclohexene-1-ol (CHol) and traces of 2-cyclohexene-1-one (CHone) (<7 %) observed at the end of the reaction.



Scheme 4. Cyclohexene epoxidation catalysed by molybdenum complexes.

In cyclohexene oxide, the ring tension is bigger than in cyclooctene oxide thus leading to the faster ring opening process in aqueous media and formation of *trans*-cyclohexane-1,2-diol. The catalytic profile on Figure 21., the reaction catalysed by the POM hybrid, shows that the quantity of cyclohexene oxide starts to decrease after 20 min, while at the same time quantity of diol increases. After 90 min, a small amount of 2-cyclohexene-1-ol is formed as a result of the allylic oxidation reaction. Overall mass balance decreases through the time due to the aqueous solubility of diol and transfer into the water phase, leading the selectivity loss as well.

After the catalytic experiments, the reaction mixtures were left open on air at room temperature in order to confirm the presence of CHD in the water phase. After a few days, white crystals were isolated, washed with Et_2O and analysed by IR spectroscopy. Obtained IR spectrum indicated the presence of cyclohexene-1,2-diol. Additionally, ^1H NMR analysis confirmed the diol presence.

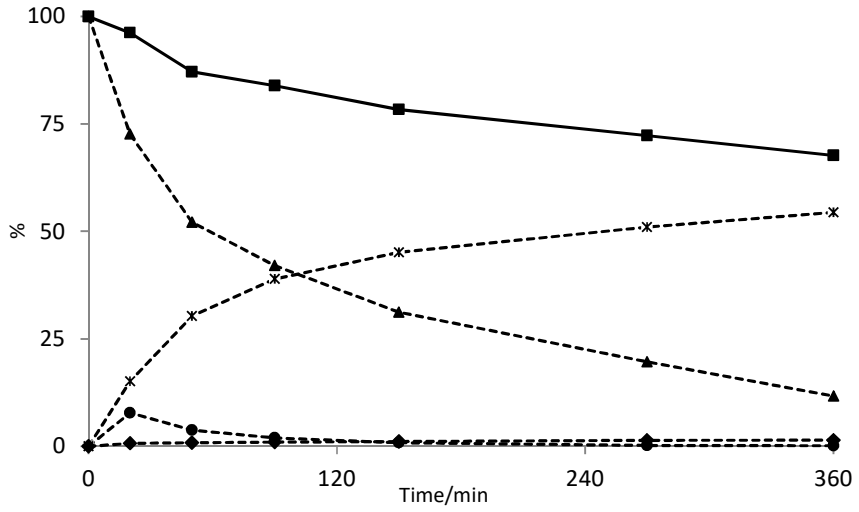


Figure 21. Conversion of cyclohexene (---▲---), formation of cyclohexene oxide (---●---), *trans*-cyclohexene-1,2-diol (---∗---) and 2-cylohexene-1-ol (---◆---), and mass balance (–■–) *vs*. time for POM hybrid catalyst, $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$. Reaction conditions: catalyst/cyclohexene/TBHP molar ratio: 0.05/100/200, T = 353K.

The results of cyclohexene epoxidation are shown in Table 6. All polynuclear and mononuclear complexes show similar conversion, selectivity, TOF and TON values. After six hours, conversions of cyclohexene are ~70 % with low epoxide selectivities (<6 %) and higher diol selectivities (~50 %). The lowest cyclohexene conversion (69 %) and diol selectivity (48 %) is obtained by the mononuclear complex [MoO_2(5MeO-SalTSC)(MeOH)]. The TOF values are lower than in cyclooctene oxidation reactions (the lowest one 718 h^{-1}). [MoO_2(H5MeO-SalTSC-4-Me)(CH_3CN)]$_2Mo_6O_{19}$ hybrid shows the best catalytic parameters with conversion up to 88 %, moderate to high diol selectivity (62 %) and highest TOF and TON values (1103 h^{-1} and 3559, respectively).

Table 6. Results of the cyclohexene epoxidation catalysed with Mo(VI) complexes in the presence of aqueous TBHP at 80 °C.

	Conv. CH / %	Selectivity (epoxide) / %	Selectivity (diol) / %	TOF_{20min} / h^{-1}	TON
[MoO_2(5MeO-SalTSC-4-Ph)]$_n$	73	0.1	53	997	1419
[MoO_2(5MeO-SalTSC-4-Me)]$_n$	71	4	50	824	1394
[MoO_2(5MeO-SalTSC)]$_n$	74	3	50	718	1459
[MoO_2(5MeO-SalTSC-4-Me)(MeOH)]	70	2	51	1046	1416
[MoO_2(5MeO-SalTSC)(MeOH)]	69	6	48	968	1361
[MoO_2(H5MeO-SalTSC-4-Me)(CH_3CN)]$_2Mo_6O_{19}$	88	0.1	62	1103	3559

Since complexes with different ligand substituents show similar kinetic profiles (Figure 22), the general conclusion is that ligand influence on the catalysis is not significant. The difference between kinetic profiles of the polynuclear and mononuclear complexes with $H_2$5MeO-SalTSC-4-Me and $H_2$5MeO-SalTSC ligands (Figure 23) is not significantly pronounced. For that reason experiments with methanol addition were not performed. On the other hand, as expected, hybrid polyoxomolybdate complex again shows the best activity (Figure 22).

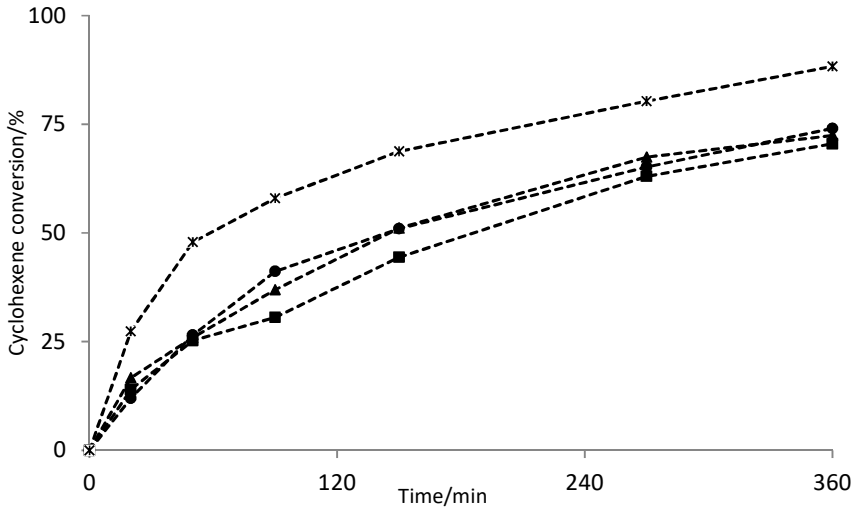


Figure 22. Converted cyclohexene *vs*. time with polynuclear dioxomolybdenum(VI) complexes and POM hybrid complex: ▲ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$, ■ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$, ● $[MoO_2(5MeO\text{-}SalTSC)]_n$ and ∗ $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$. Reaction conditions: catalyst/cyclohexene/TBHP molar ratio: 0.05/100/200, T = 353 K.

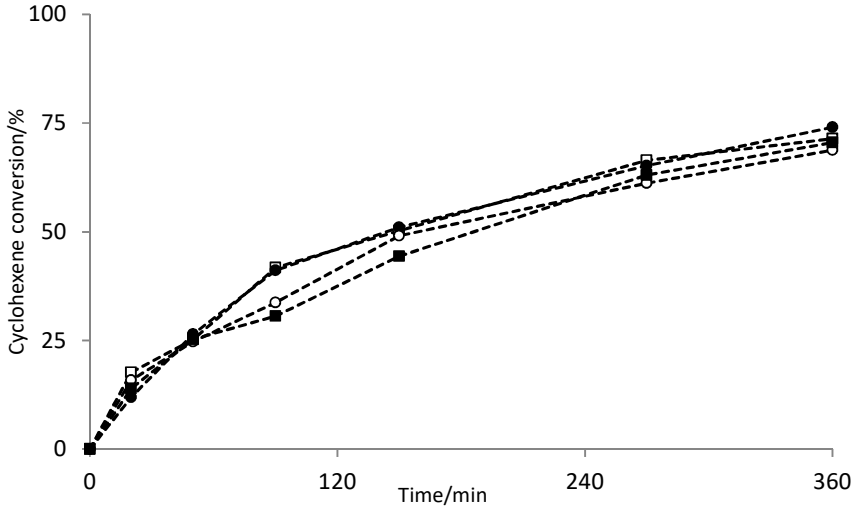
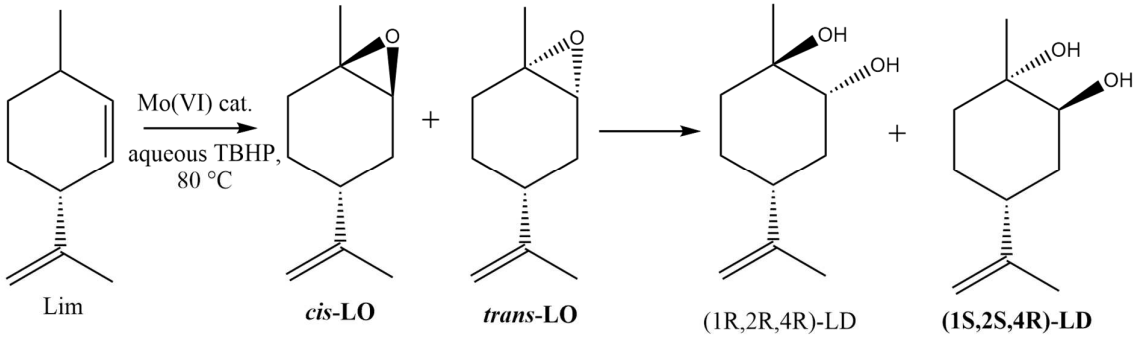


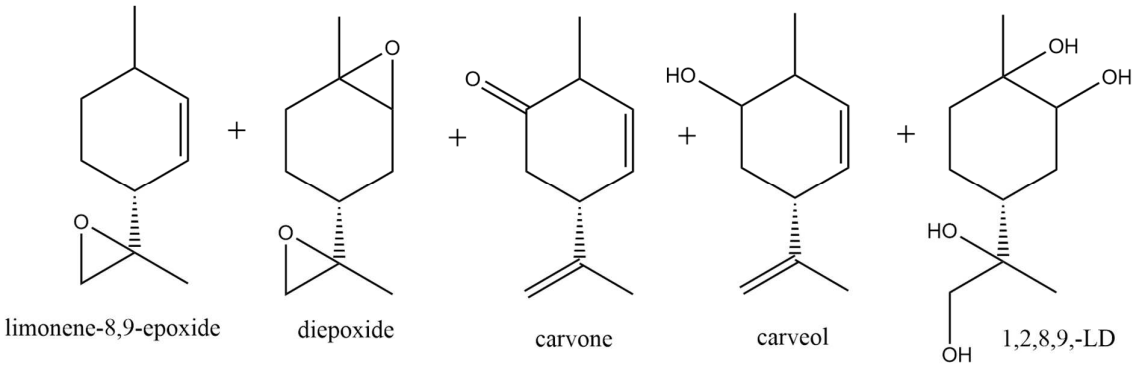
Figure 23. Converted cyclohexene *vs*. time with polynuclear and mononuclear dioxomolybdenum(VI) complexes: ■ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$, ● $[MoO_2(5MeO\text{-}SalTSC)]_n$, □ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$, ○ $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$. Reaction conditions: catalyst/cyclohexene/TBHP molar ratio: 0.05/100/200, T = 353 K.

4.3.3. Epoxidation of (R)-limonene

Unlike previous substrates, epoxidation of limonene (Lim) is much more complicated since it has two different alkene moieties. Depending upon reaction conditions and the catalyst used, a lot of various products can be obtained. In most cases, *cis*- and *trans*-limonene oxides (*cis*-LO, *trans*-LO) are produced as a result of preferential endocyclic double bond epoxidation. In the aqueous media, oxides can be easily transformed into corresponding diols, (1R,2R,4R)-LD and (1S,2S,4R)-LD due to the epoxide ring opening process (Scheme 5). Less abundant products are limonene-8,9-epoxide, diepoxide and other compounds such as carvone and carveol resulting from the allylic oxidation reaction (Scheme 6).



Scheme 5. Solvent-free epoxidation of (*R*)-limonene catalysed by molybdenum complexes with usual products of epoxidation.



Scheme 6. Other potential but less abundant products of limonene epoxidation.

Molybdenum catalysed epoxidation of limonene yielded three main products found in the organic phase: *cis*-LO, *trans*-LO and (1S,2S,4R)-LD (Scheme 5). Also, a small amount of one unidentified product was observed after 90 min, presumably (1R,2R,4R)-LD. Besides the main products, traces of carvone and carveol were identified, but not quantified.

According to Figure 24, at the beginning of the reaction small amount of *cis*-LO and *trans*-LO is formed. A quantity of the *cis*-LO decreases very fast in contrast to the *trans*-LO, while at the same time quantity of (1R,2R,4R)-LD increases rapidly. This suggests that the ring opening of *cis*-LO is faster and selectively leads to the (1S,2S,4R)-LD production. As expected, overall mass balance is decreasing during the reaction due to the diol solubility in the water phase. After 6 hours significant loss of material is observed. This can also be attributed to the production of various products detected in gas-chromatography and many of them are water soluble.

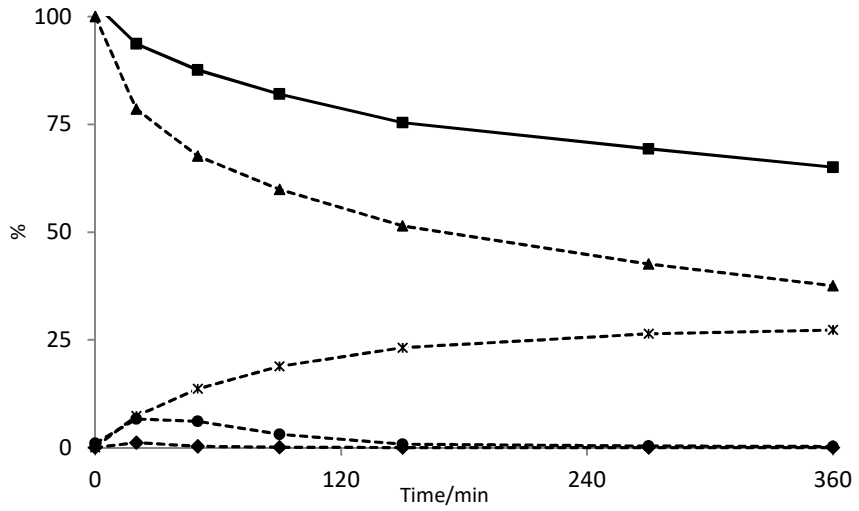


Figure 24. Conversion of limonenene (---▲---), formation of *cis*-limonene oxide (---◆---), *trans*-limonene oxide (---●---), (1S,2S,4R)-limoenene diol (···∗···) and mass balance (–■–) *vs*. time for the polynuclear catalyst, $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$. Reaction conditions: catalyst/limonene/TBHP molar ratio: 0.05/100/200, T = 353K.

Results of catalysis are compiled in Table 7. Epoxidation of limonene yielded moderate to high conversion values (58-83 %), however low considering other substrates. Very high TOF and TON values are obtained by the use of POM hybrid (2169 h^{-1} and 3323, respectively). On the other hand, selectivities are very low especially towards *trans*-LO (<1 %).

Table 7. Results of the limonene epoxidation catalysed with Mo(VI) complexes in the presence of aqueous TBHP at 80 °C.

	Conv. Lim / %	Selectivity (*trans*-LO) / %	Selectivity [(1S,2S,4R)-LD] / %	TOF_{20min} / h^{-1}	TON
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$	62	0.4	44	1241	1241
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$	66	0.5	44	1819	1302
$[MoO_2(5MeO\text{-}SalTSC)]_n$	58	0.8	39	1191	1141
$[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$	70	0.4	41	1844	1386
$[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$	63	0.5	44	1593	1280
$[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$	83	0.1	43	2169	3323

Comparing the kinetic profiles of the polynuclear and mononuclear complexes with different ligands (Figure 25 and 26, respectively) it seems that complexes with 5MeoSalTSC-4-Me ligand have better catalytic activity in the epoxidation of limonene.

Also, it seems that mononuclear complexes $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$ and $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$ are better than the corresponding polynuclear ones (Figure 26). This could suggest that polynuclear complexes are more likely to be found in dinuclear or oligonuclear soluble form in the solution. If so, access of the TBHP oxidant molecule to the catalytically active pentacoordinated intermediate is slower than in mononuclear catalyst. As in cyclooctene and cyclohexene epoxidation, POM hybrid catalyst shows far better kinetic profile than the rest of complexes (Figure 25) along with selectivity, TOF and TON values.

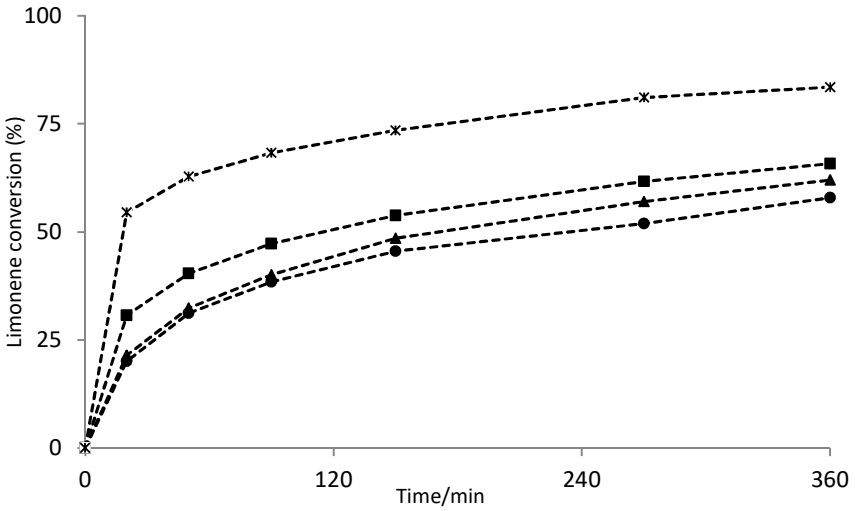


Figure 25. Converted limonene *vs*. time with polynuclear dioxomolybdenum(VI) complexes and POM hybrid complex: ▲ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$, ■ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$, ● $[MoO_2(5MeO\text{-}SalTSC)]_n$ and ∗ $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$. Reaction conditions: catalyst/limonene/TBHP molar ratio: 0.05/100/200, T = 353 K.

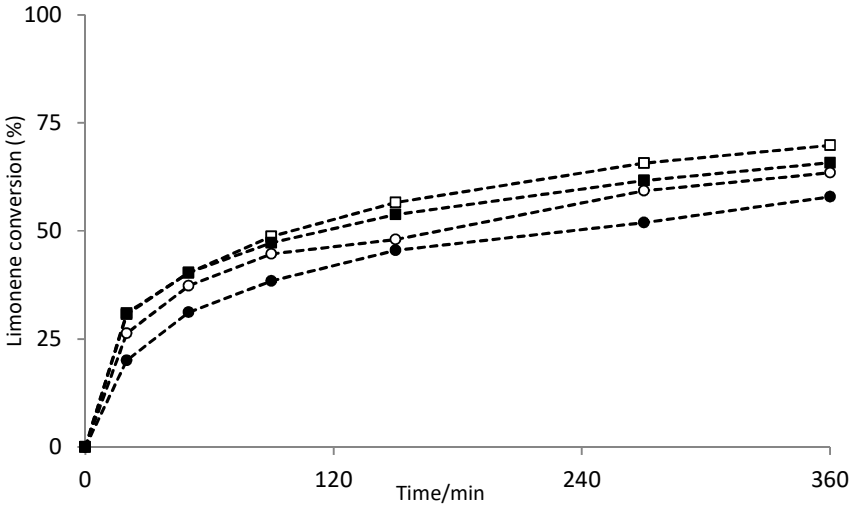


Figure 26. Converted limonene *vs*. time with polynuclear and mononuclear dioxomolybdenum(VI) complexes: ■ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$, ● $[MoO_2(5MeO\text{-}SalTSC)]_n$, □ $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$, ○ $[MoO_2(5MeO\text{-}SalTSC)(MeOH)]$. Reaction conditions: catalyst/limonene/TBHP molar ratio: 0.05/100/200, T = 353 K.

§ 5. CONCLUSION

In this diploma thesis polynuclear $[MoO_2(5\text{-MeO-SalTSC-4-Ph})]_n$, $[MoO_2(5\text{-MeO-SalTSC-4-Me})]_n$, $[\{MoO_2(5\text{-MeO-SalTSC})\}\cdot ½CH_3CN]_n$ and mononuclear $[MoO_2(5\text{-MeO-SalTSC-4-Me})(MeOH)]$, $[MoO_2(5\text{-MeO-SalTSC})(MeOH)]\cdot MeOH$ dioxomolybdenum(VI) complexes and hybrid organic-inorganic polyoxomolybdate complex $[MoO_2(H5\text{-MeO-SalTSC-4-Me})(CH_3CN)]_2Mo_6O_{19}$ have been synthesized and characterized. In these complexes, *cis*-$\{MoO_2\}^{2+}$ core is coordinated to the thiosemicarbazone ligand through the oxygen, nitrogen and sulphur atom in doubly deprotonated form (polynuclear and mononuclear complexes) and monodeprotonated form (POM hybrid complex). The sixth coordination site is occupied by the oxygen atom from the neighbouring complex molecule or by the methanol molecule. The complex cation of POM hybrid compound contains coordinated acetonitrile molecule. It has been established that complexes $[MoO_2(5MeO\text{-SalTSC})(MeOH)]\cdot(MeOH)$ and $[\{MoO_2(5\text{-MeO-SalTSC})\}\cdot ½CH_3CN]_n$ lose additional solvent molecule by standing at room temperature.

Molybdenum(VI) complexes were tested as (pre)catalyst in the solvent-free epoxidation of *cis*-cyclooctene, cyclohexene and (*R*)-limonene. Complexes have shown to be very efficient and cyclooctene was found to be the best modal substrate for epoxidation reactions where cyclooctene oxide was obtained as the only product. High values of conversions and selectivities were obtained (~83 and ~91, respectively). Catalytic test for cyclohexene was less successful due to the *trans*-cyclohexene-1,2-diol formation and loss of selectivity. Likewise, (*R*)-limonene epoxidation yielded low epoxide selectivity as a result *cis*- and *trans*-limonene oxide hydrolysis and production of various undetected products. However, in tested conditions, cyclohexene and limonene conversions were moderate to good (69-88 % and 58-83 %, respectively). Since the complexes with different ligand substituents showed similar kinetic parameters, the general conclusion was that ligand influence on the catalysis is not significant. Also, reactions after methanol addition did not affect the kinetic profiles significantly. Considering the type of complex used, POM hybrid showed the best activity. This result was expected since the complex has two potential active sites, the $[MoO_2(HL^2)]^+$ cation and $Mo_6O_{19}^{2-}$ anion.

§ 6. LIST OF ABBREVIATIONS AND SYMBOLS

$H_2$5MeO-SalTSC- 5-methoxysalicylaldehyde thiosemicarbazone

$H_2$5MeO-SalTSC-4-Ph- 5-methoxysalicylaldehyde 4-phenylthiosemicarbazone

$H_2$5MeO-SalTSC-4-Me- 5-methoxysalicylaldehyde 4-methylthiosemicarbazone

acac- acetylacetonate

CH- cyclohexene

CHD- cyclohexene diol

CHO- cyclohexene oxide

CHol- 2-cyclohexane-1-ol

CHone- 2-cyclohexene-1-one

CO- *cis*-cyclooctene

D-donor molecule

GC- gas-chromatography

IR- infrared

L- ligand

Lim- (*R*)-limonene

LD- limonene diol

LO- limonene oxide

MeOH- methanol

POM- polyoxometalate (polyoxomolybdate)

SalTSC- salicylaldehyde thiosemicarbazone

TBHP- *tert*-butyl hydroperoxide

TOF- turn-over frequency

TON- turn-over number

TSC- thiosemicarbazone

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§ 8. APPENDIX

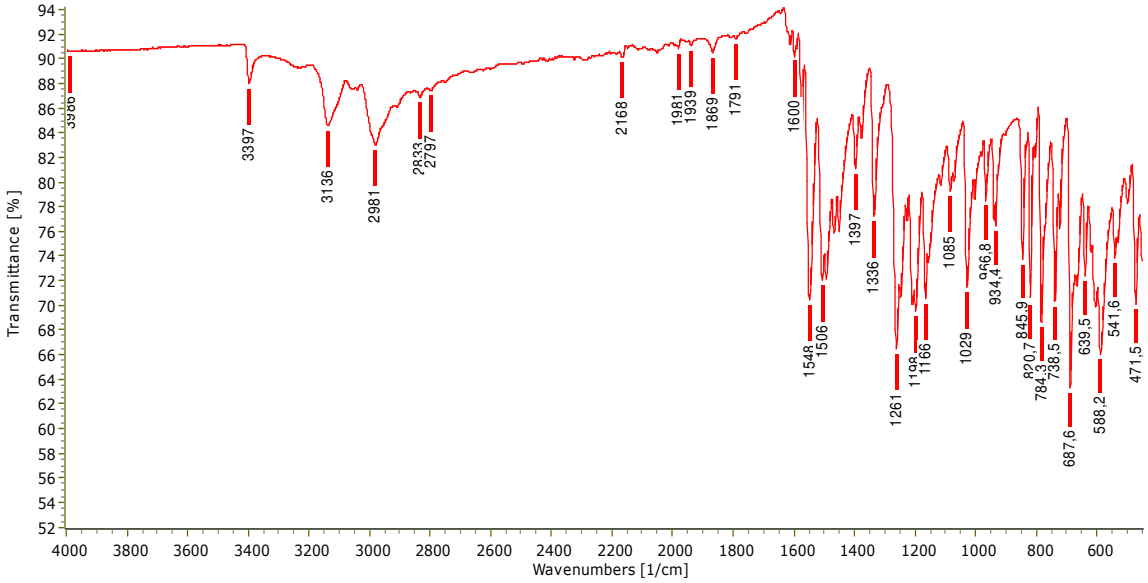

Figure D1. IR spectrum of ligand $H_2$5MeO-SalTSC-4-Ph.

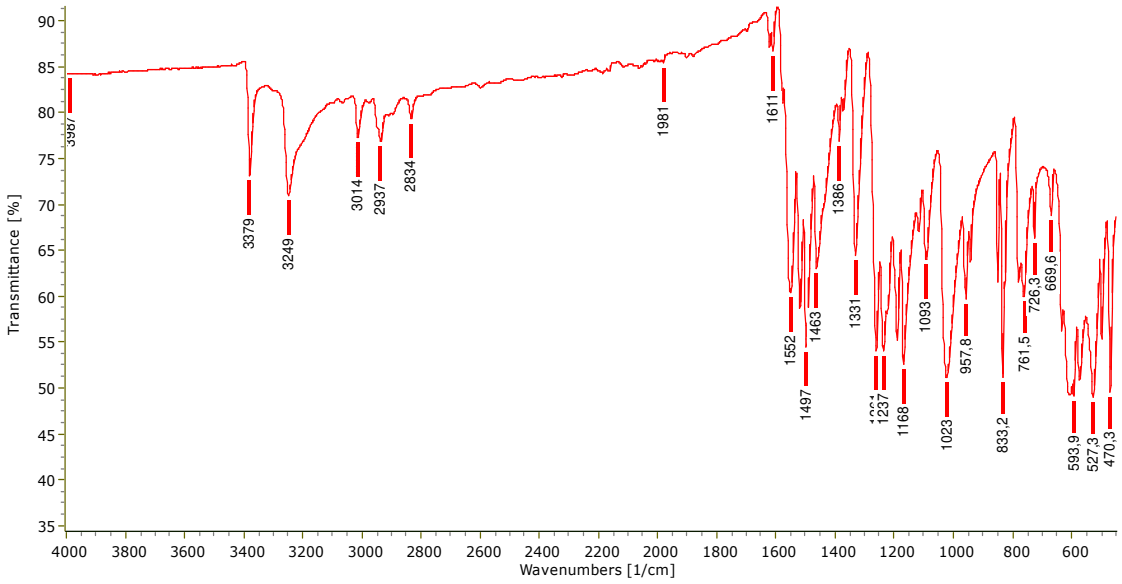

Figure D2. IR spectrum of ligand $H_2$5MeO-SalTSC-4-Me.

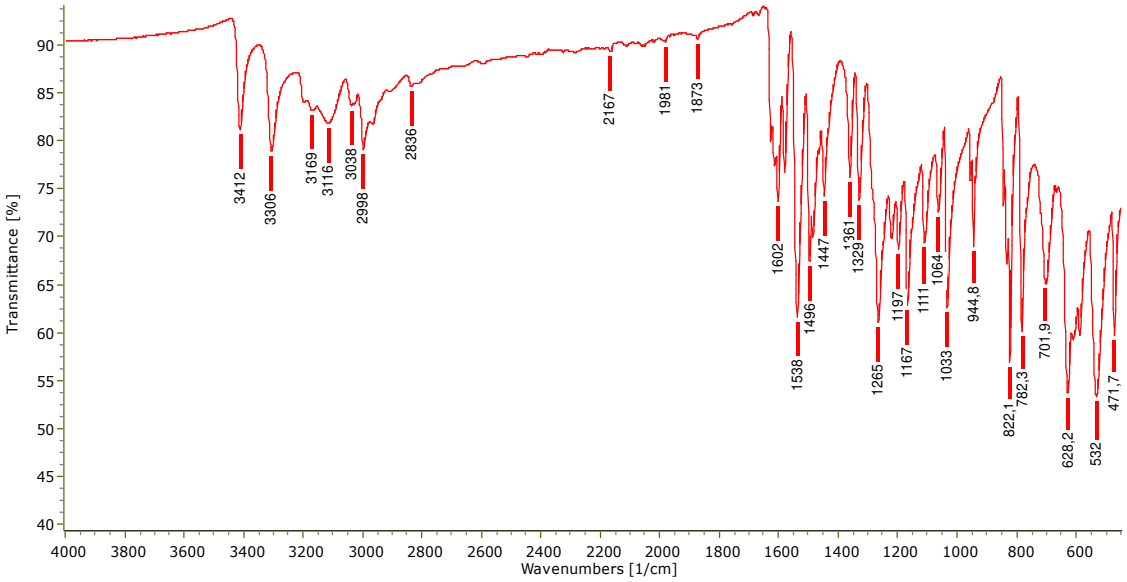

Figure D3. IR spectrum of ligand $H_2$5MeO-SalTSC.

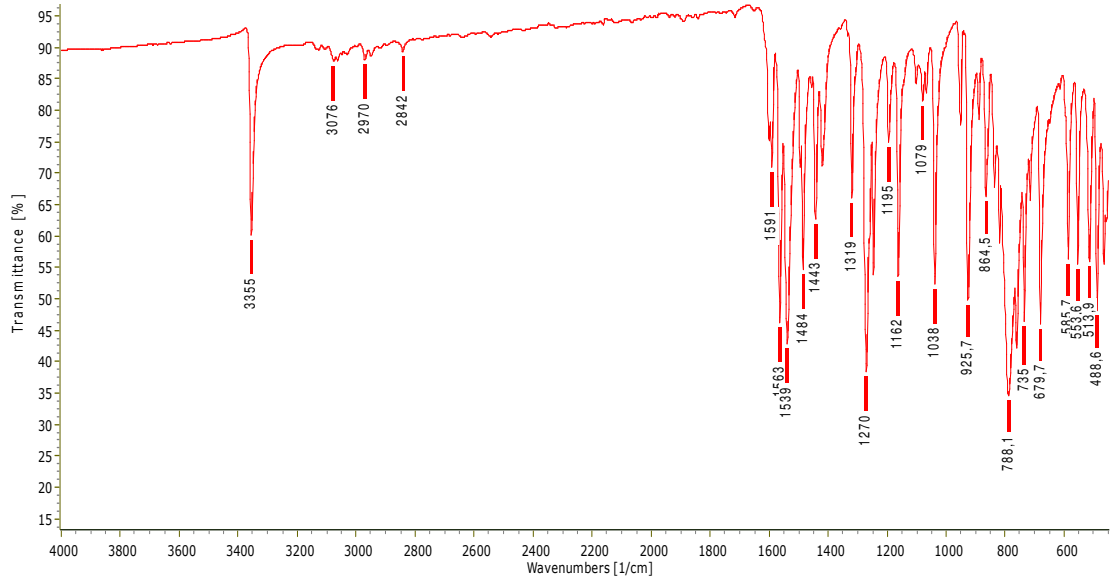

Figure D4. IR spectrum of the complex $[MoO_2$(5MeO-SalTSC-4-Ph)$]_n$.

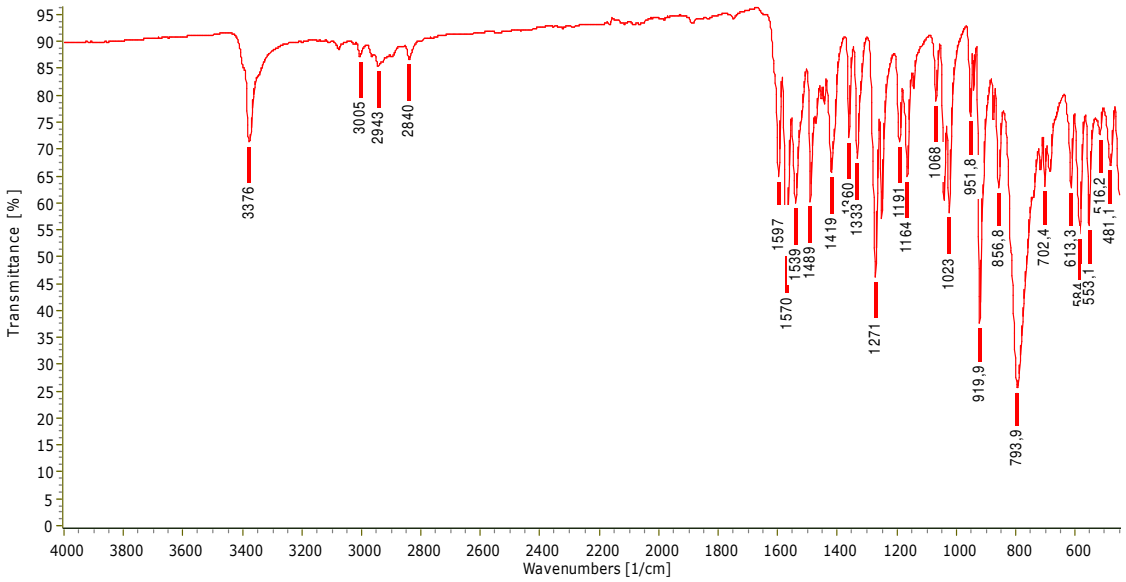

Figure D5. IR spectrum of the complex $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$.

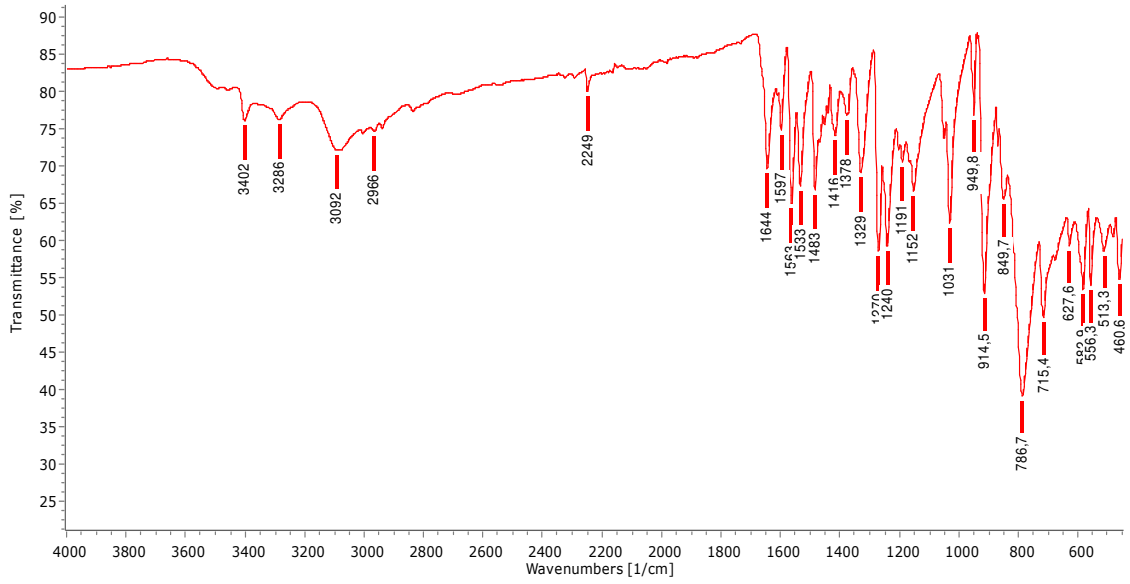

Figure D6. IR spectrum of the complex $[\{MoO_2(5\text{-}MeO\text{-}SalTSC)\}\cdot ½CH_3CN]_n$.

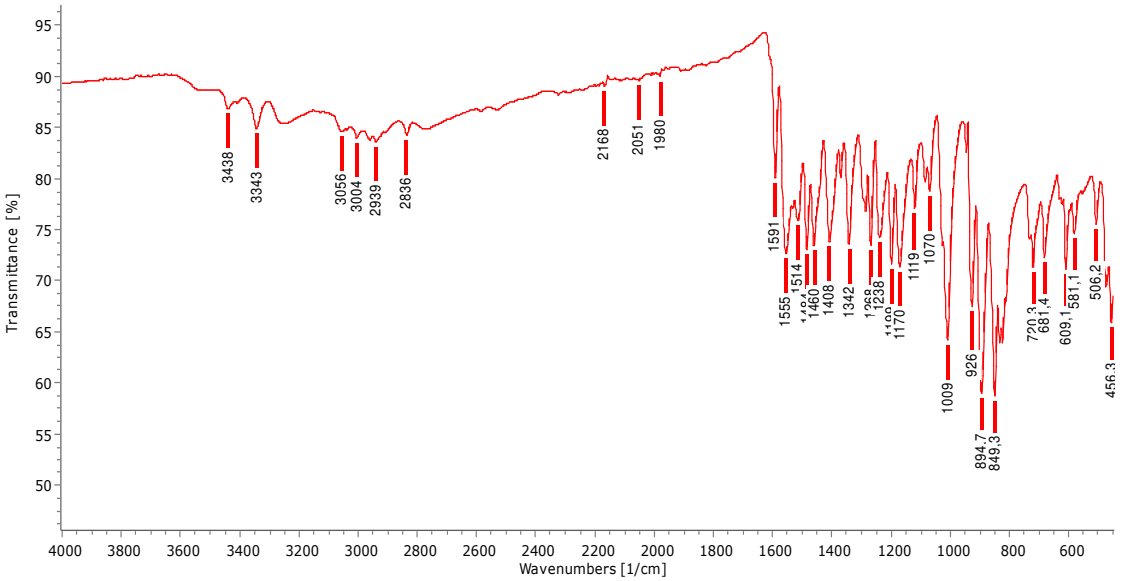

Figure D7. IR spectrum of the complex [MoO_2(5MeO-SalTSC-4-Me)(MeOH)].

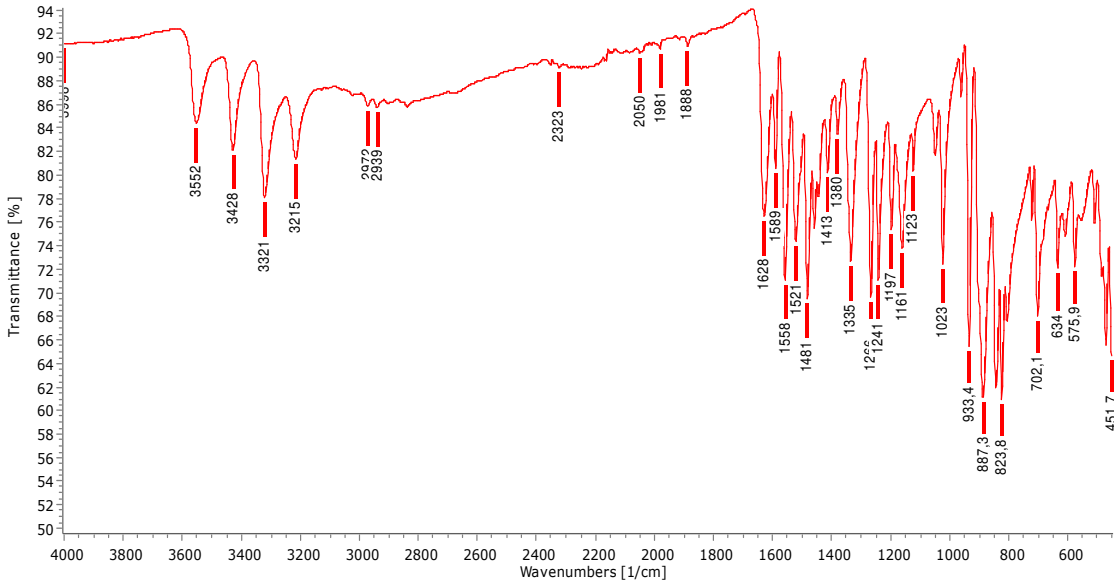

Figure D8. IR spectrum of the complex [MoO_2(5MeO-SalTSC)(MeOH)].

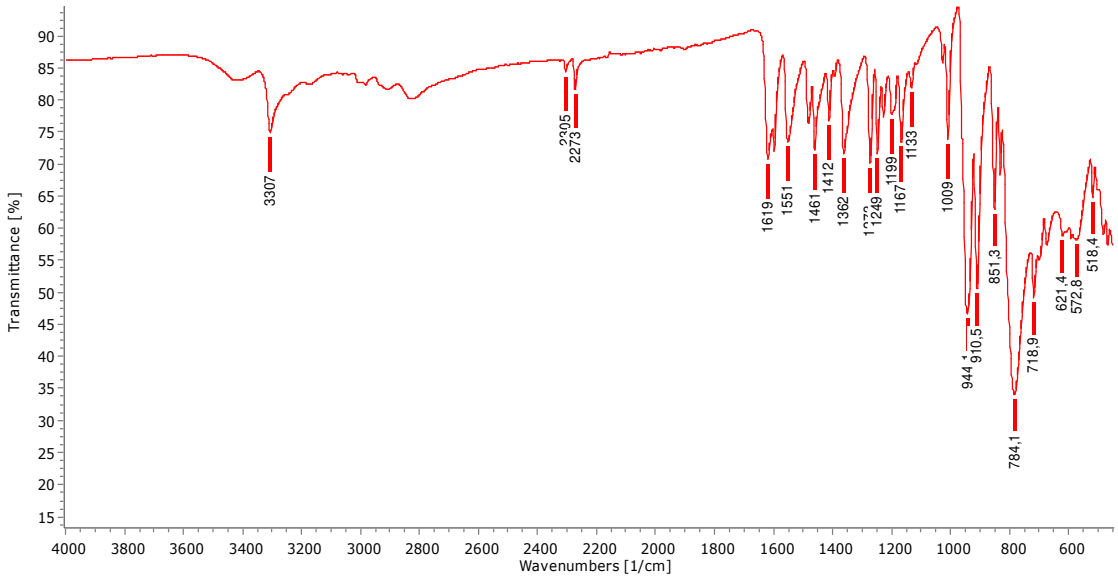

Figure D9. IR spectrum of the complex $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$.

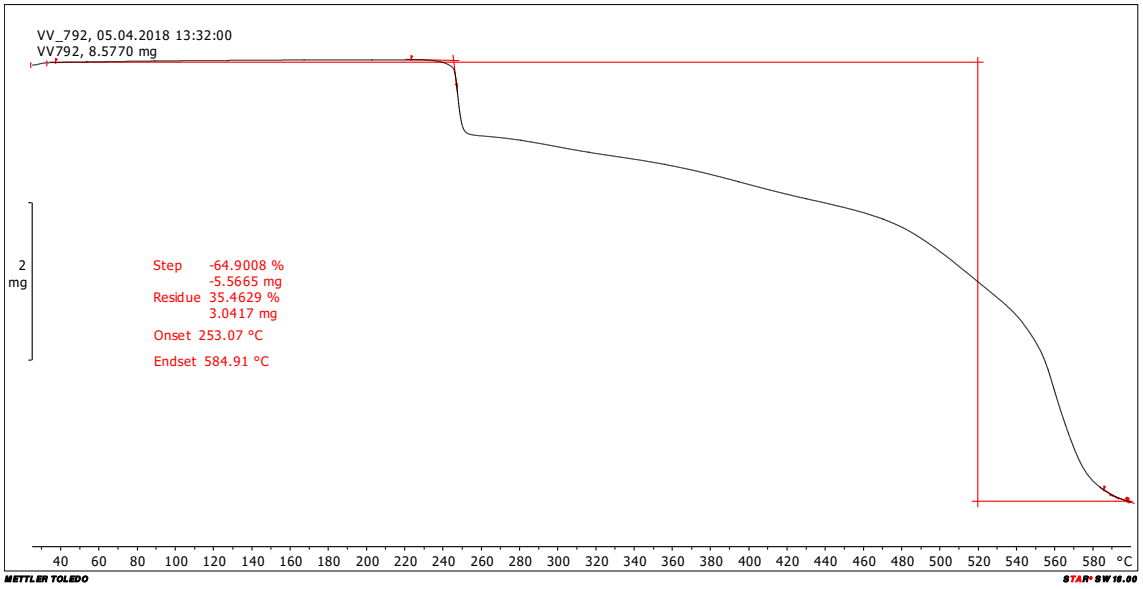

Figure D10. Thermogram of the complex $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$.

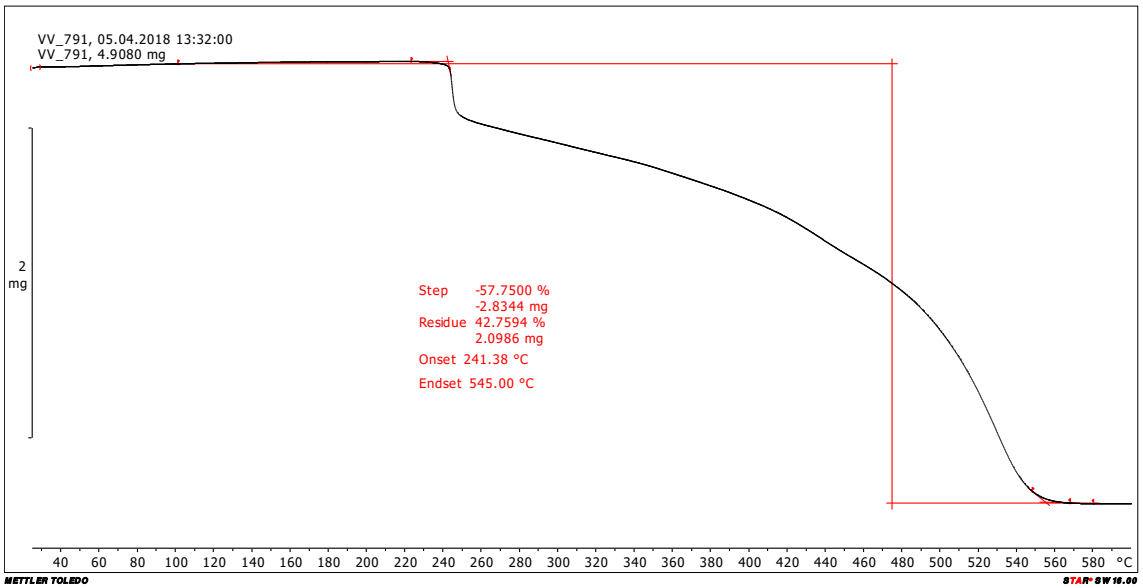

Figure D11. Thermogram of the complex $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$.

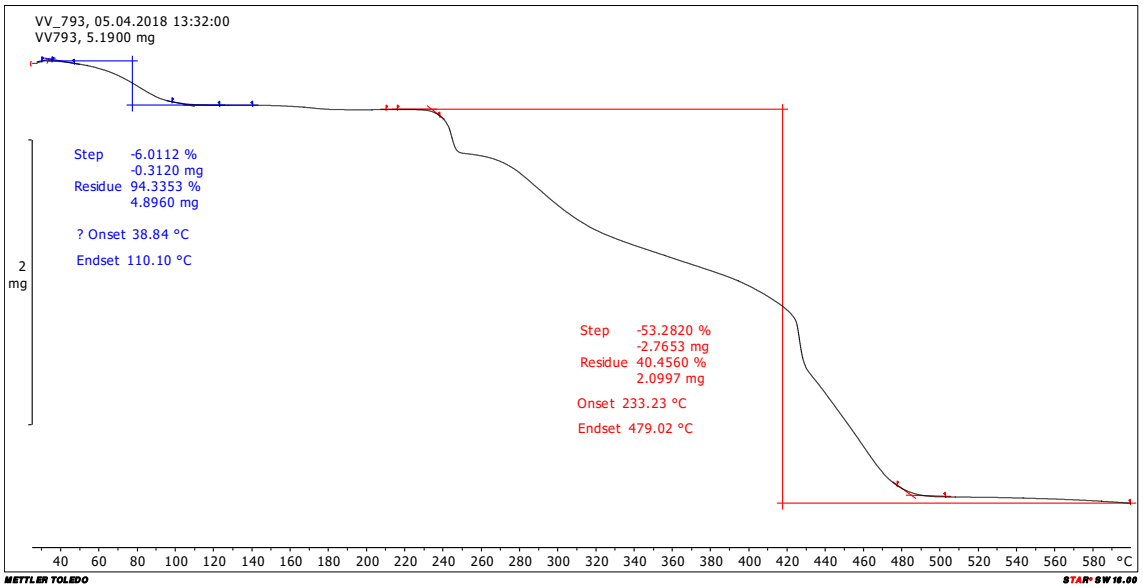

Figure D12. Thermogram of the complex $[\{MoO_2(5\text{-}MeO\text{-}SalTSC)\}\cdot ½CH_3CN]_n$.

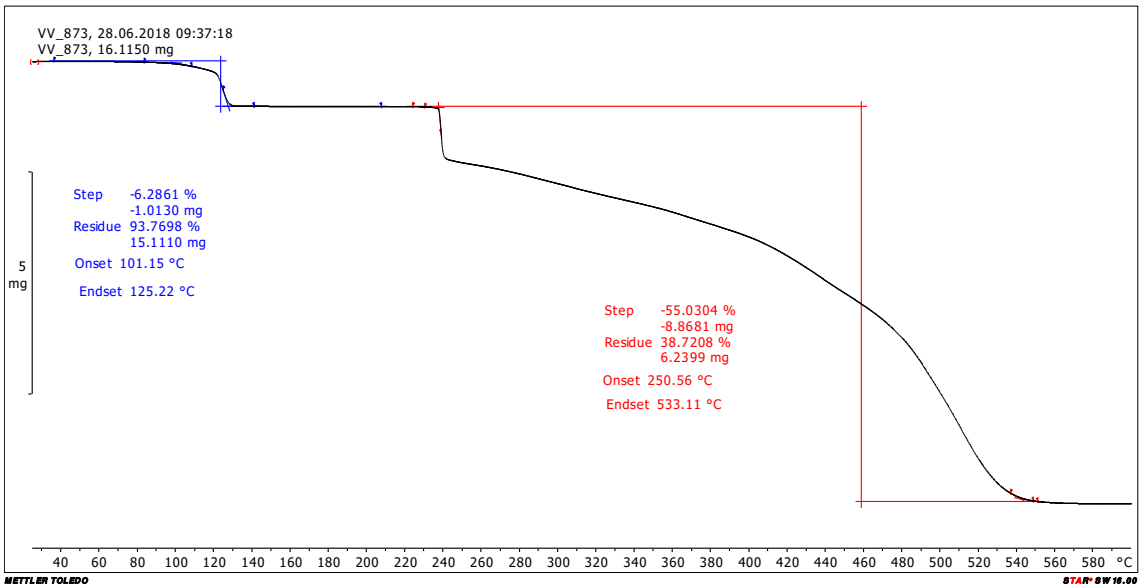

Figure D13. Thermogram of the complex [MoO_2(5MeO-SalTSC-4-Me)(MeOH)].

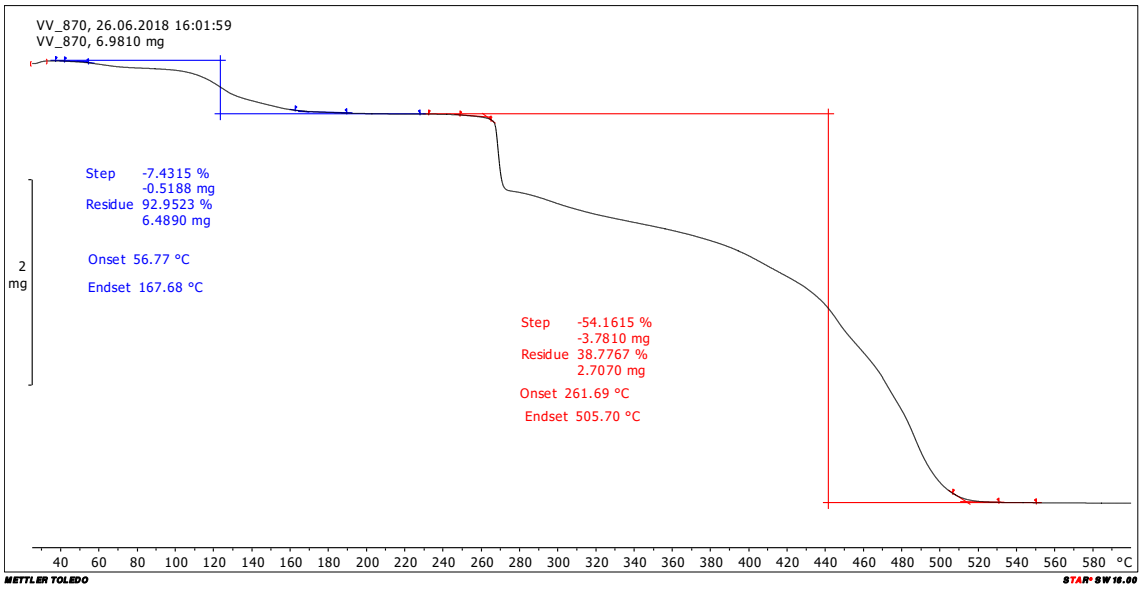

Figure D14. Thermogram of the complex [MoO_2(5MeO-SalTSC)(MeOH)].

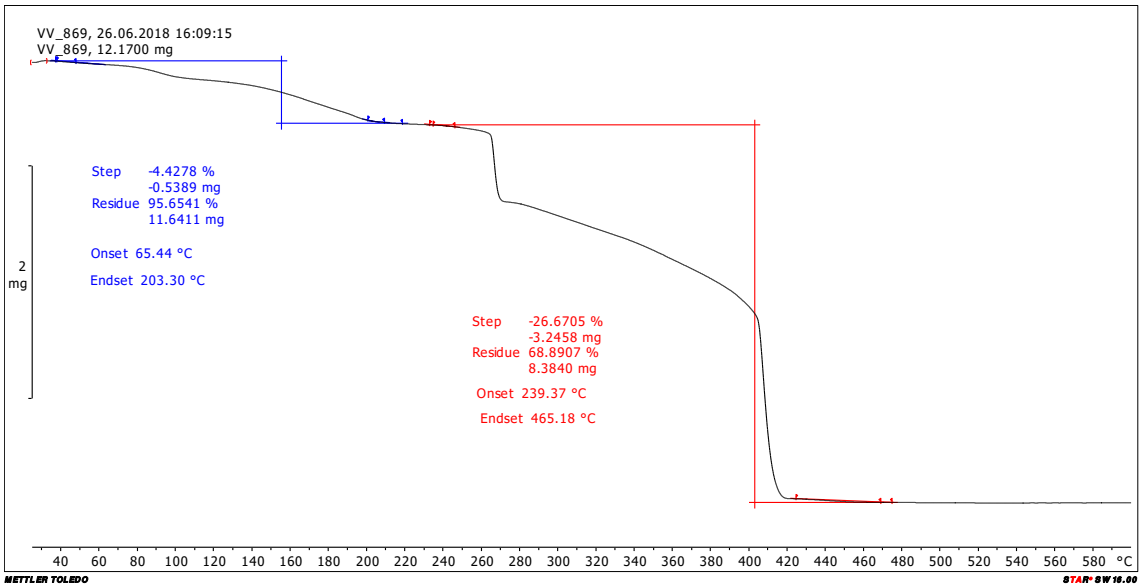

Figure D15. Thermogram of the complex $[MoO_2(H5MeO\text{-}SalTSC\text{-}4\text{-}Me)(CH_3CN)]_2Mo_6O_{19}$.

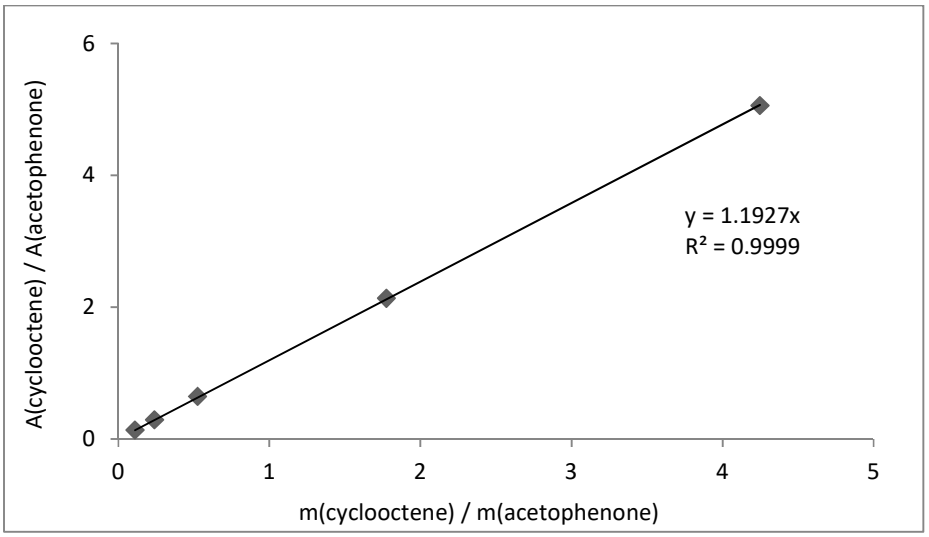

Figure D16. Calibration curve of cyclooctene obtained by GC measurement with acetophenone as an internal standard.

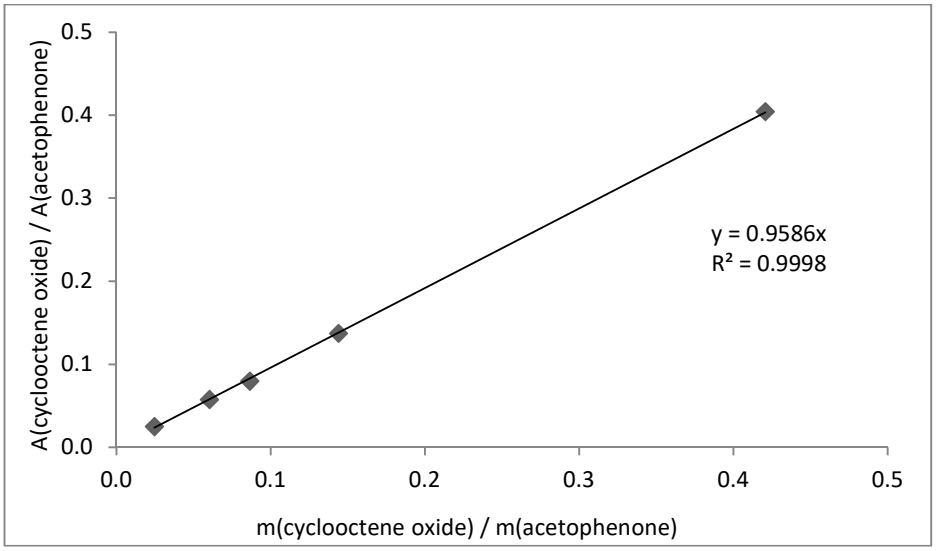

Figure D17. Calibration curve of cyclooctene oxide obtained by GC measurement with acetophenone as an internal standard.

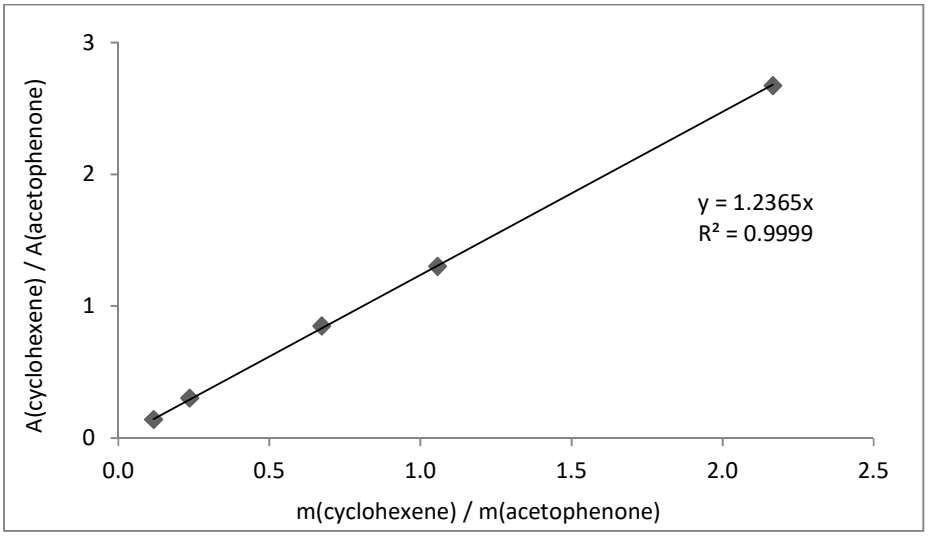

Figure D18. Calibration curve of cyclohexene obtained by GC measurement with acetophenone as an internal standard.

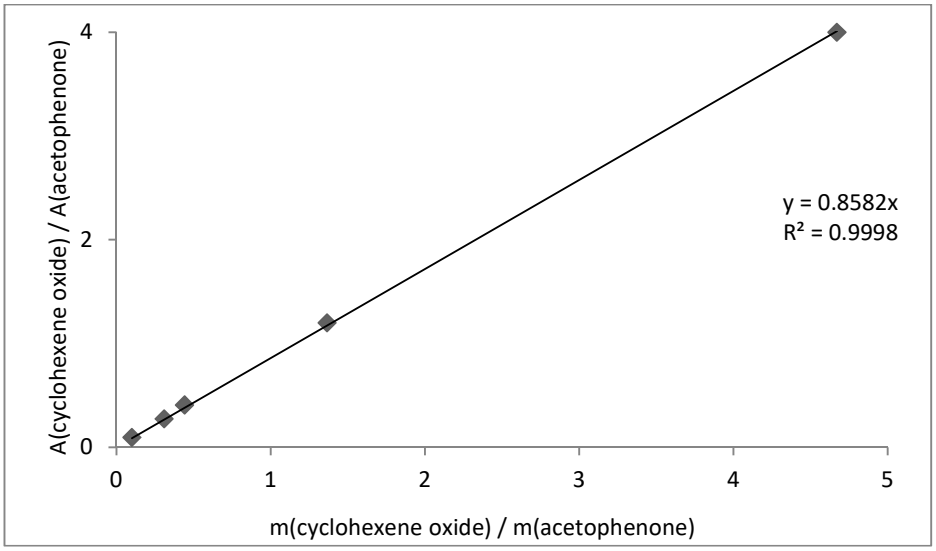

Figure D19. Calibration curve of cyclohexene oxide obtained by GC measurement with acetophenone as an internal standard.

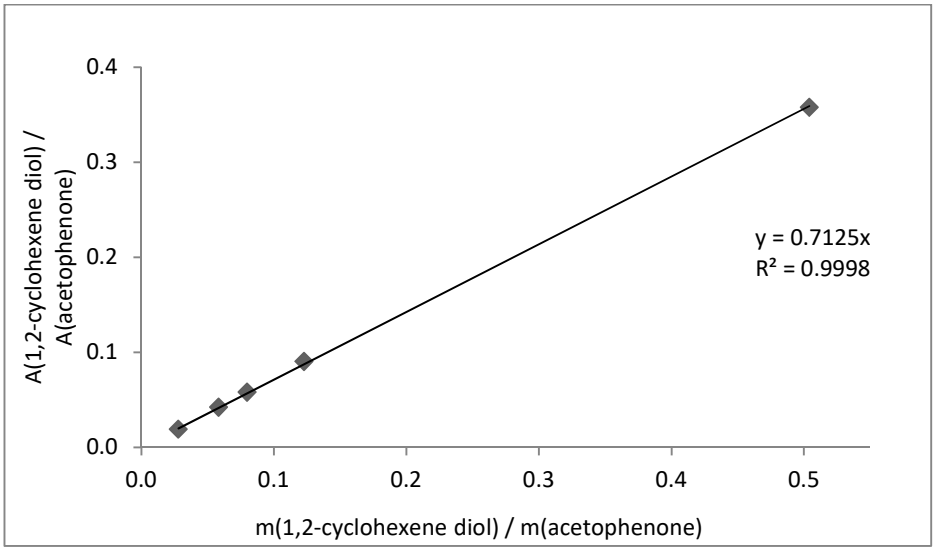

Figure D20. Calibration curve of 1,2-cyclohexane diol obtained by GC measurement with acetophenone as an internal standard.

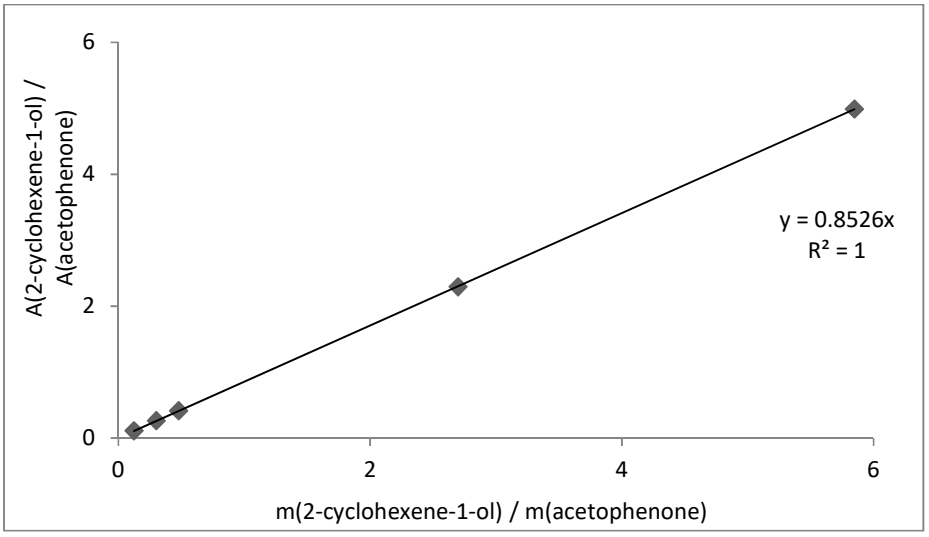

Figure D21. Calibration curve of 2-cyclohexene-1-ol obtained by GC measurement with acetophenone as an internal standard.

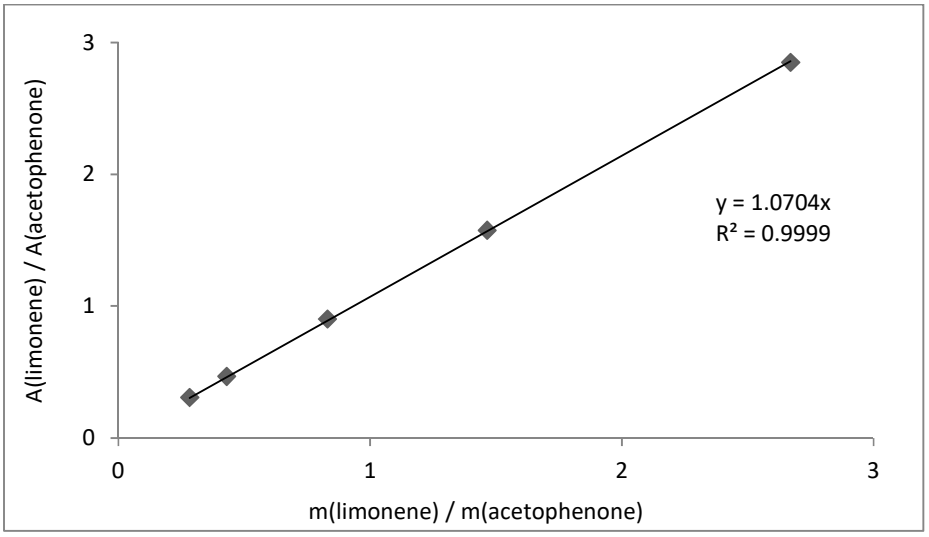

Figure D22. Calibration curve of limonene obtained by GC measurement with acetophenone as an internal standard.

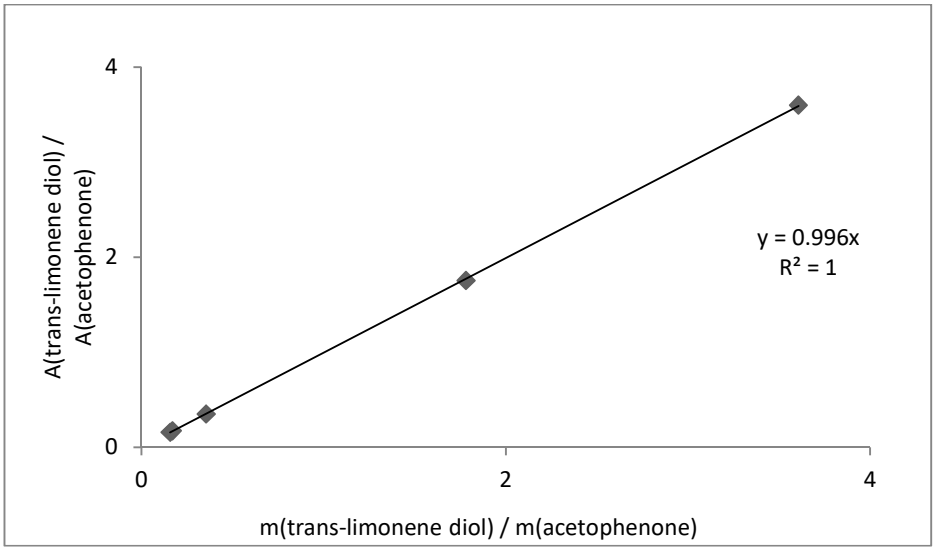

Figure D23. Calibration curve of *trans*-limonene oxide obtained by GC measurement with acetophenone as an internal standard.

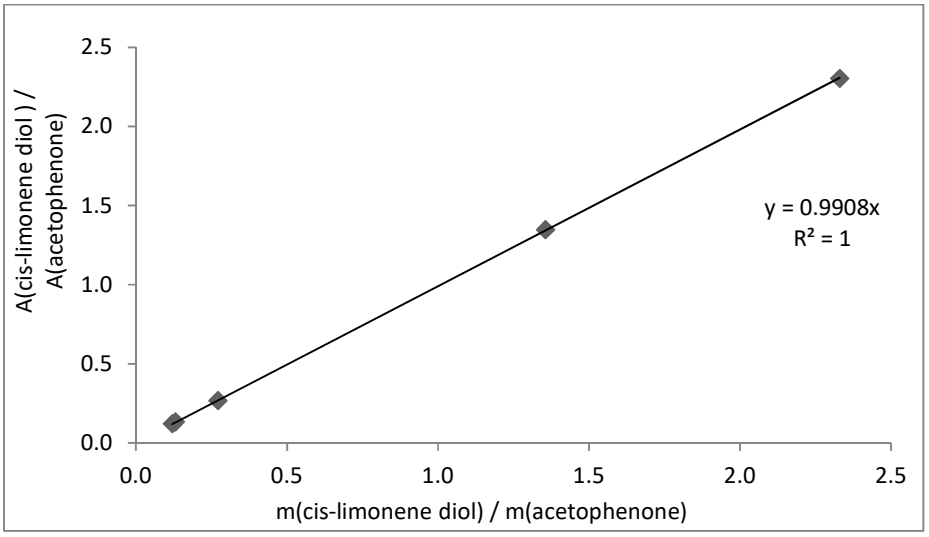

Figure D24. Calibration curve of *cis*-limonene oxide obtained by GC measurement with acetophenone as an internal standard.

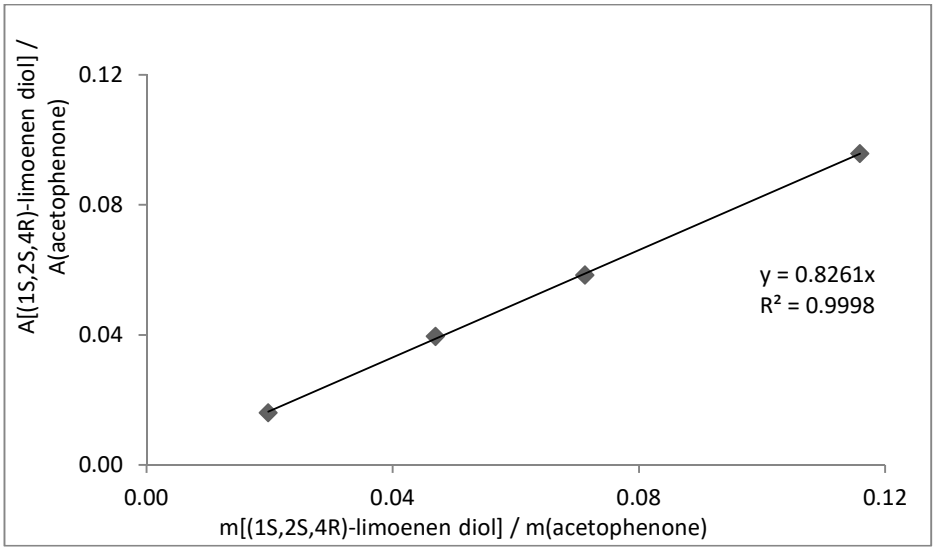

Figure D25. Calibration curve of (1S,2S,4R)-limonene diol obtained by GC measurement with acetophenone as an internal standard.

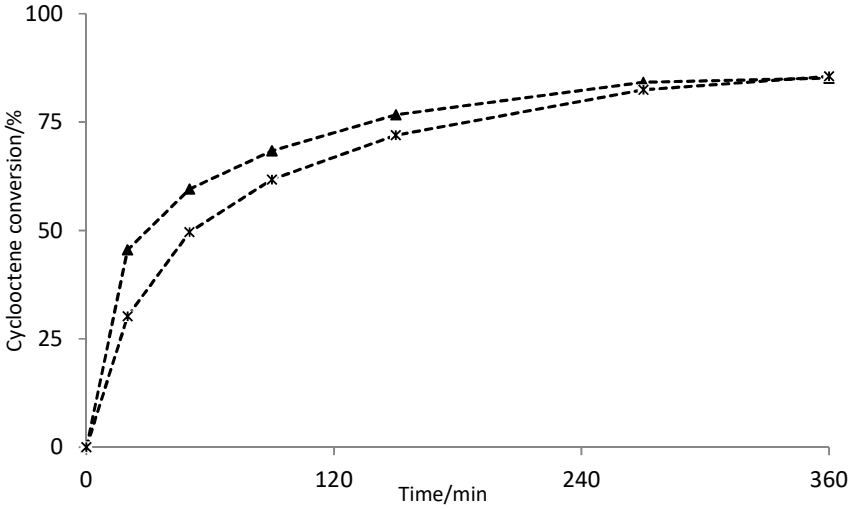

Figure D26. Converted cyclooctene *vs*. time with dioxomolybdenum(VI) complex derived from the 5MeO-SalTSC-4-Ph ligand. Kinetic profiles present polynuclear complex $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Ph)]_n$ (▲) and the profile of the reaction after addition of MeOH (1 μL) (∗) to the polynuclear complex at the beginning of the reaction. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.05/100/200, T = 353 K.

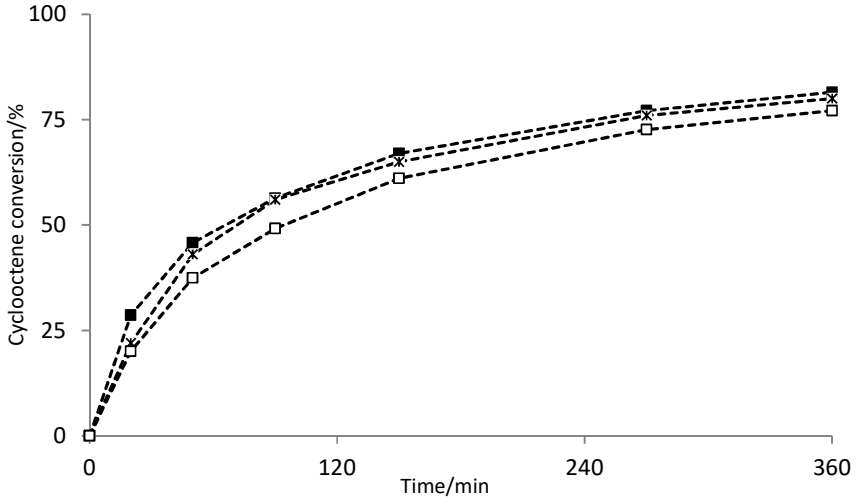

Figure D27. Converted cyclooctene *vs*. time with dioxomolybdenum(VI) complexes derived from the 5MeO-SalTSC-4-Me ligand. Kinetic profiles present polynuclear $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$ (■) and mononuclear complexes $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$ (□) and the profiles of the reaction after addition of MeOH (1 μL) (∗) to the polynuclear complex at the beginning of the reaction. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.05/100/200, T = 353 K.

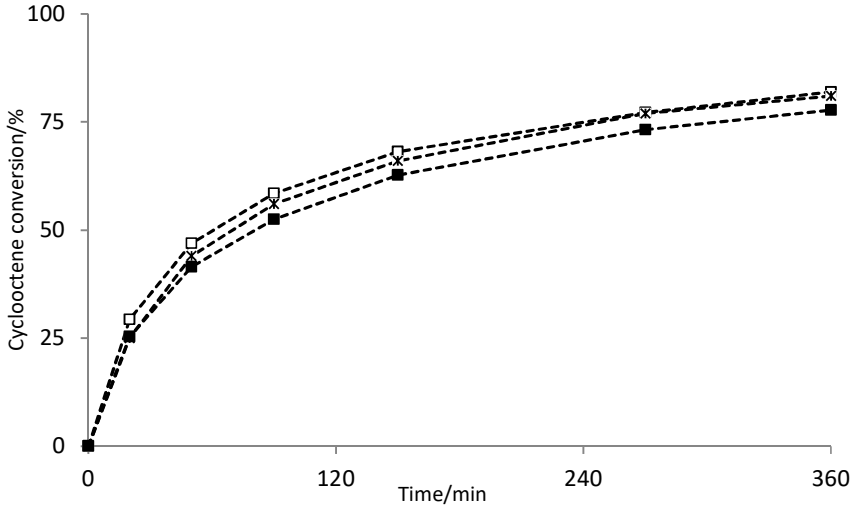

Figure D28. Converted cyclooctene *vs*. time with dioxomolybdenum(VI) complexes derived from the 5MeO-SalTSC ligand. Kinetic profiles present polynuclear $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)]_n$ (■) and mononuclear complexes $[MoO_2(5MeO\text{-}SalTSC\text{-}4\text{-}Me)(MeOH)]$ (□) and the profiles of the reaction after addition of MeOH (1 μL) (∗) to the polynuclear complex at the beginning of the reaction. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.05/100/200, T = 353 K.

§ 9. CURRICULUM VITAE

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Place of birth: Ogulin

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2001–2009	Elementary School Ivan Goran Kovačić, Vrbovsko
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2013–2018	Undergraduate Studies in Chemistry, Faculty of Science, University of Zagreb
2018	Erasmus+ Internship, CNRS-LCC/IUT, Castres

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Participation in the organization of Open day of Chemistry