Synthesis and catalytic activity of novel molybdenum hydrazonato complexes

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SYNTHESIS AND CATALYTIC ACTIVITY OF NOVEL MOLYBDENUM HYDRAZONATO COMPLEXES

Diploma Thesis

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This Diploma Thesis was performed at Division of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb under mentorship of Assistant Professor 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

SYNTHESIS AND CATALYTIC ACTIVITY OF NOVEL MOLYBDENUM HYDRAZONATO COMPLEXES

Marta Razum

As part of this diploma thesis, solution-based and mechanochemical syntheses of hydrazone compounds, obtained from 2,3-dihydroxybenzaldehyde and 2- or 4-aminobenzhydrazide (H_2L^1 and H_2L^2), was performed. Two dinuclear dioxomolybdenum(VI) complexes, $[MoO_2L]_2$, and two mononuclear complexes, $[MoO_2L(MeOH),]$ have been synthesised by the reaction of $[MoO_2(acac)_2]$ and corresponding hydrazone ligand H_2L in 1:1 molar ratio. Mononuclear complexes $[MoO_2L(MeOH)]$ were obtained from methanol solution, while dinuclear complexes $[MoO_2L]_2$ from acetonitrile one. Complexes were characterised by IR and NMR spectroscopies and analysed by TG and elemental analyses. The catalytic activity of all complexes was tested under organic solvent-free for the epoxidation of *cis*-cyclooctene and oct-1-ene with three different oxidants, aqueous *tert*-butyl hydroperoxide, *tert*-butyl hydroperoxide in decane and hydrogen peroxide, with the emphasis on the low catalyst loading (0.25 mol% *vs*. substrate).

(61 pages, 49 figures, 6 tables, 23 references, original in English)

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SAŽETAK

SINTEZA I KATALITIČKA AKTIVNOST HIDRAZONSKIH KOMPLEKSA MOLIBDENA

Marta Razum

U sklopu ovog diplomskog rada izvedene su otopinske i mehanokemijske sinteze hidrazonskih spojeva, priređenih iz 2,3-dihidroksibenzaldehida i 2- ili 4-aminobenzhidrazida (H_2L^1 i H_2L^2). Dva dinuklearna kompleksa dioksomolibdena(VI), $[MoO_2L]_2$ i dva mononuklearna kompleksa $[MoO_2L(MeOH)]$ sintetizirani su reakcijom $[MoO_2(acac)_2]$ i odgovarajućeg hidrazonskog liganda H_2L u molarnom omjeru 1:1. Mononuklearni kompleksi $[MoO_2L(MeOH)]$ dobiveni su iz otopine metanola, dok dinuklearni kompleksi $[MoO_2L]_2$ iz acetonitrila. Kompleksi su karakterizirani IR i NMR spektroskopijom i analizirani TG i elementarnim analizama. Katalitička aktivnost svih kompleksa ispitana je epoksidacijom *cis*-ciklooktena i okt-1-ena bez dodatka organskih otapala u reakcijski medij, s tri različita oksidansa, vodenom otopinom *tert*-butil hidroperoksida, *tert*-butil hidroperoksidom u dekanu i vodikovim peroksidom, s naglaskom na mali udio katalizatora (0,25 mol.% u odnosu na supstrat).

(61 stranica, 49 slika, 6 tablica, 23 literaturnih navoda, jezik izvornika: engleski)

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Ključne riječi: *cis*-ciklookten, epoksidacija, hidrazoni, kompleksi molibdena(VI)

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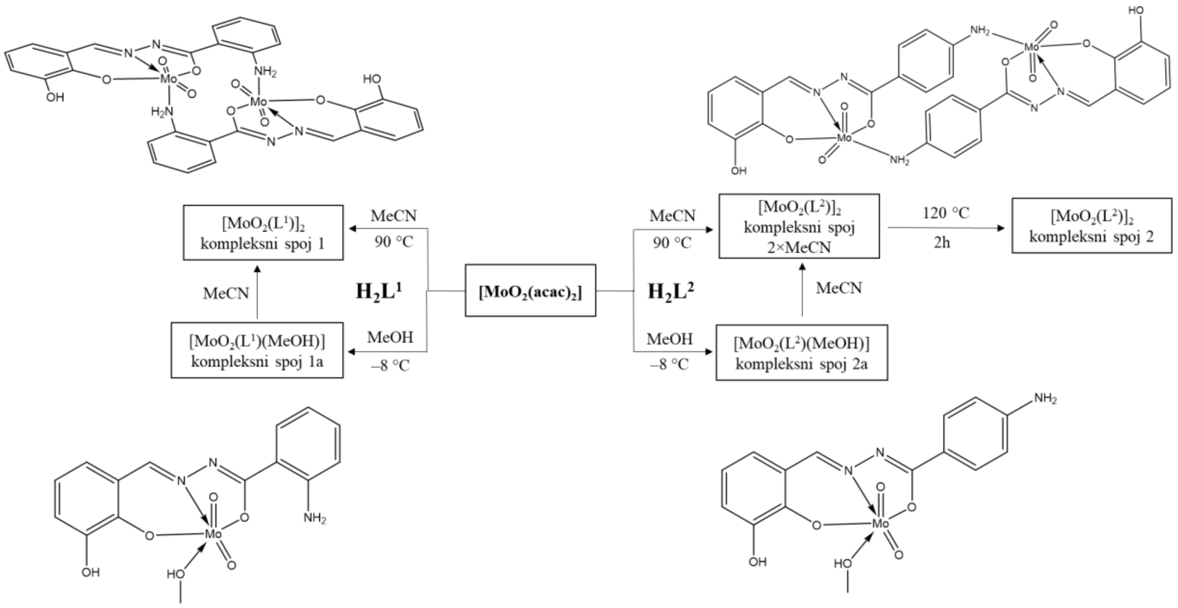
PROŠIRENI SAŽETAK

Molibden je jedan od rijetkih elemenata s vrlo dobro istraženom ulogom u biološki važnim procesima živih organizama, a da pripada skupini prijelaznih elemenata druge ili treće periode. Većina enzima molibdena sudjeluje u reakcijama prijenosa kisika. Pored svoje biološke važnosti, molibdenski kompleksi pronašli su svoju ulogu u reakcijama katalitičke oksidacije raznovrsnih supstrata. Radi boljeg razumijevanja oksidacijskih svojstava molibdena(VI), provedena su mnoga istraživanja sa velikim brojem različitih liganada koordiniranih na metalni centar.

Kompleksni spojevi molibdena(VI) uobičajeno su pripravljeni reakcijom $[MoO_2(acac)_2]$ ili $[MoO_2Cl_2]$ s odgovarajućim hidrazonskim ligandom u metanolu, etanolu ili acetonitrilu, a sastoje se od *cis*-$\{MoO_2\}^{2+}$ jezgre i tridentatnog *ONO* liganda koordiniranog preko fenolnog kisika, imino-dušika i enolnog kisika. Tri najčešća tipa kompleksnih spojeva dioksomolibden(VI) s *ONO* tipom hidrazonskog liganda su mononuklearni $[MoO_2(L)(D)]$, gdje L^{2-} odgovara ligandu, a D je molekula donora, dinuklearni $[MoO_2(L)]_2$ i polinuklearni $[MoO_2(L)]_n$ kompleksni spojevi. Koordinacija oko molibdenskog centra je oktaedarska. U slučaju mononuklearnog kompleksnog spoja šesto mjesto koordinacije zauzima molekula donora (D), dok u polinuklearnim i dinuklearnim kompleksnim spojevima 6. koordinacijsko mjesto može biti zauzeto atomom kisika iz Mo=O jedinice susjedne molekule ili nekim drugim atomom donorom ili skupinom prisutnom na ligandu. Atom donor je u većini slučajeva N ili O, a donorska skupina OH ili NH_2.

U ovom diplomskom radu predstavljena je sinteza i karakterizacija kompleksnih spojeva molibdena(VI) s dva različita aminohidrazonska liganda, 2-amino-(2,3-dihidroksibenziliden)benzhidrazid (H_2L^1) i 4-amino-(2,3-dihidroksibenziliden)benzhidrazid (H_2L^2) te je ispitana njihova katalitička aktivnost u reakcijama epoksidacije olefina.

U reakciji $[MoO_2(acac)_2]$ s odgovarajućim ligandom dobiveni su mononuklearni i dinuklearni kompleksni spojevi (shema 1). Mononuklearni kompleksni spojevi, $[MoO_2(L)(MeOH)]$, dobiveni su iz otopine metanola, a dinuklearni, $[MoO_2(L)]_2$, iz acetonitrila. Svi kompleksni spojevi su karakterizirani IR i NMR spektroskopijom, te termogravimetrijskom i elementnom analizom.



Shema 1. Prikaz dobivenih dinuklearnih i mononuklearnih molibden(VI) kompleksnih spojeva

Infracrvenom spektroskopijom utvrđeno je postojanje vrpca karatkterističnih za istezanja $C{=}N_{imino}$ (1602-1614 cm^{-1}), $C\text{-}O_{fenil}$ (1240-1263 cm^{-1}), $C\text{-}O_{hidrazon}$ (1325-1347 cm^{-1}) veza. Uz navedene vrpce u spektrima mononuklearnih kompleksnih spojeva uočena je vrpca karakteristična za metanol (1022 cm^{-1}) te vrpca karakteristična za $Mo\text{-}O_{MeOH}$ (878-893 cm^{-1}) istezanja. Kod dinuklearnih kompleksnih spojeva prisutna je vrpca karakteristična za istezanje Mo-N (879-859 cm^{-1}) veze čime je potvrđeno da je došlo do dimerizacije kompleksnog spoja preko dušikovog atoma prisutnog na ligandu susjedne molekule.

Termogravimetrijskom (TG) analizom oba mononuklearna kompleksna spoja određena je prisutnost molekule metanola te potvrđena koordinativno kovalentna veza metanolnog kisika i molibdenskog centra. TG analizom dinuklearnog kompleksnog spoja s 4-amino-(2,3-dihidroksibenziliden)benzhidrazidom kao ligandom uočena je prisutnost molekule acetonitrila koja je prisutna u kristalnoj strukturi.

Pripremljeni kompleksni spojevi ispitani su kao (pred)katalizatori u epoksidaciji olefina u uvjetima bez dodatka organskog otapala. U reakcijama epoksidacije *cis*-ciklooktena i okt-1-ena, vodena otopina *tert*-butil hidroperoksida (TBHP), TBHP u dekanu i vodikov peroksid korišteni su kao oksidansi. Ciklookten se široko primjenjuje kao modelni supstrat za reakcije epoksidacije olefina i produkt tih reakcija je odgovarajući epoksid. Korištenjem manje reaktivnog olefina kao supstrata, npr. okt-1-en, uočava se veća razlika u aktivnosti Mo(VI) kompleksnih spojeva.

Katalitičke reakcije pokazale su da je ciklookten bolji supstrat u odnosu na okt-1-en, gledano u odnosu na selektivnost prema željenom produktu, odgovarajućem epoksidu. Najveće vrijednosti pretvorbe ciklooktena (99 %) dobivene su u reakcijama u kojima je TBHP u dekanu korišten kao oksidans, vjerojatno zbog velike topljivosti kompleksa u reakcijskoj smjesi. U reakcijama s vodenom otopinom TBHP-a uočena je mala razlika u pretvorbi među kompleksnim spojevima (89 % - 94 %), dok su u reakcijama s H_2O_2 kao oksidansom vrijednosti pretvorbe ciklooktena vrlo male (6 % - 12 %) Također na temelju svih prikupljenih podataka dinuklearni kompleksni spojevi pokazali su veće vrijednosti pretvorbe ciklooktena od mononuklearnih. Razlog uočenog je jednostavnije stvaranje mononuklearnih pentakoordiniranih $[MoO_2L]$ vrsta zbog slabe veze koordinirane amino skupine i Mo atoma. Na temelju dobivenih katalitičkih rezultata, može se primijetiti da položaj amino skupine na fenilnom prstenu utječe na katalitička svojstva kompleksnih spojeva, te kompleksni spojevi s 2-aminobenzoilhidrazonom pokazuju bolju katalitičku aktivnost od kompleksnih spojeva s 4-aminobenzoilhidrazonom.

§ 1. INTRODUCTION

Molybdenum is one element among the few second and third-row transition elements with a known activity in living organisms. The vast majority of molybdenum-containing enzymes participate in oxygen transfer reactions, forming or breaking bonds between oxygen and carbon. Some of those enzymes contain a *cis*-dioxo Mo(VI) active site structure.[1] For a better understanding of molybdenum(VI) oxidizing properties, there has been an increase in the research of Mo(VI) complexes with a wide variety of coordinated ligands.[2–7] In addition to its biological importance, molybdenum complexes have found their catalyst role in oxidation reactions of important substrates.[8]

The complexes with MoO_2^{2+} core and tridentate ligands often present a distorted octahedral geometry around the metal, forming mononuclear, dinuclear or polynuclear structures according to the experimental procedures.[9] Those types of Mo(VI) complexes, with a labile sixth coordination site, can be especially useful in industrial-scale catalytic reactions. This is mainly related to (ep)oxidation reactions of olefins where epoxides are obtained as the product. Epoxides are very important chemicals in the synthesis of fine chemicals, pharmaceuticals, polymers.[6] In future industrial processes, it is important to follow the principles of green chemistry,[8] both for environmental protection and for economic reasons, using reasonable amounts of chemicals, solvents and energy.

In this diploma thesis, the synthesis and characterization of molybdenum(VI) complexes with two different aminohydrazone ligands H_2L are presented. In the reaction of $[MoO_2(acac)_2]$ with tridentate aminohydrazone ligand, mononuclear $[MoO_2L(MeOH)]$ and dinuclear $[MoO_2L]_2$ complexes were obtained. Mononuclear structures were obtained from methanol solution while dinuclear ones from acetonitrile. All complexes were characterized by IR and NMR spectroscopies, as well as thermogravimetric and elemental analyses. Furthermore, the prepared complexes were tested as (pre)catalysts in epoxidation of olefins under organic solvent-free conditions. In the presented epoxidation of *cis*-cyclooctene and oct-1-ene, aqueous TBHP, TBHP in decane and hydrogen peroxide were used as oxidants. All catalytic reactions were monitored by gas chromatography (GC).

§ 2. LITERATURE REVIEW

2.1. Hydrazone Schiff base ligands

Imines are compounds with the general structure $RN{=}CR^1R^2$ where R=H, with nitrogen doubly bonded to carbon. Compounds where $R{=}NH_2$ or NHR^3 are hydrazones (Figure 1).[10]

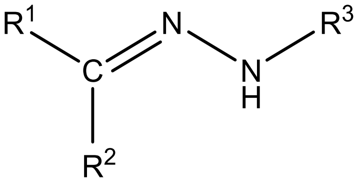
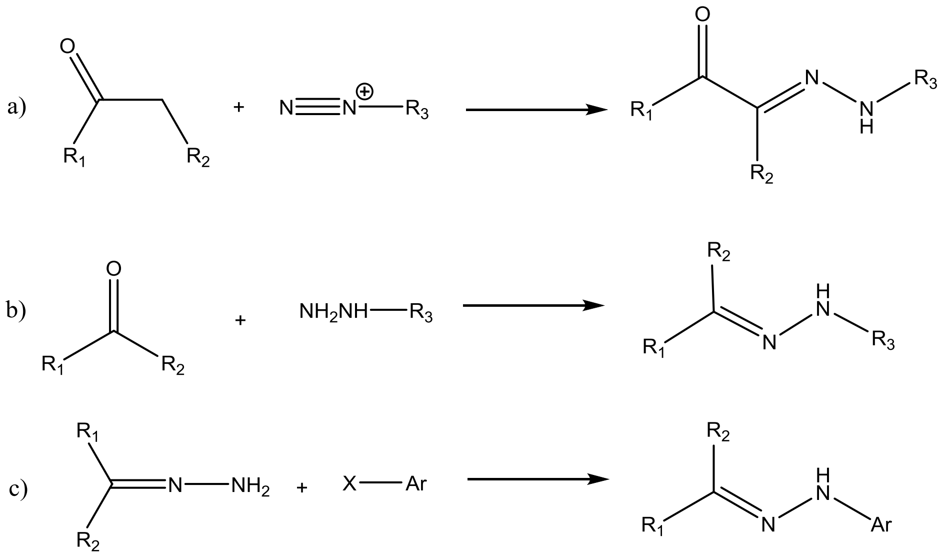


Figure 1. The basic structure of hydrazone Schiff base.

Hydrazones can be synthesized by three main synthetic pathways (Scheme 1):

- the coupling between aryl diazonium salts and *β*-keto esters or acids (Japp-Klingemann reaction),
- the coupling between hydrazines and aldehydes or ketones
- and the coupling between aryl halides and non-substituted hydrazones.[11]



Scheme 1. The synthesis of hydrazones, a) Japp-Klingemann reaction; b) hydrazine-aldehyde/ketone reaction; c) aryl halide substitution.[5]

The synthetic method applied within this thesis, is the second one, refluxing stoichiometric amounts of hydrazine and aldehyde or ketone dissolved in suitable solvent.[12]

2.1.1. Hydrazones as ONO donor ligands

Hydrazones with general formula –C(O)–NH–N=CH– are of particular interest in coordination chemistry. That kind of hydrazone ligands exhibit keto-enol tautomerism in solution (Figure 2). In the majority of reactions, the enol form undergoes complexation in the presence of metal ion.[13]

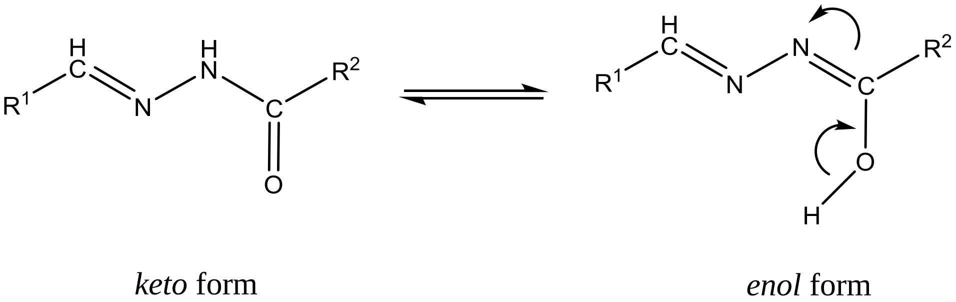


Figure 2. Keto-enol tautomerism of hydrazone ligand.

In the majority of reactions where hydrazone as *ONO* donor ligand is formed, one of the reactants is benzaldehyde with at least one hydroxyl group.[4–7,13–18] At the Figure 3, R^1 position is occupied by a different types of hydroxybenzaldehyde.

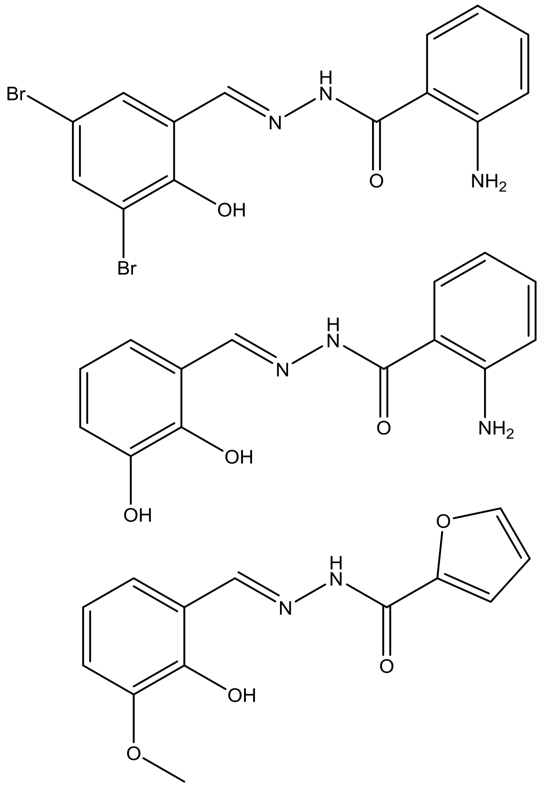


Figure 3. Some examples of hydrazone as *ONO* donor ligand.[5,6,13]

This type of hydrazone ligand behaves as a tridentate ligand in which the phenolate oxygen, the imino nitrogen and enolate oxygen occupy the meridional plane.[6,7,17,19]

Hydrazones play an important role in inorganic chemistry, as they easily form stable complexes with many transition metal ions, for example Zn^{2+}, Cu^{2+}, Ni^{2+}.[11,20] They can coordinate to the metal centre as neutral, monoprotonated or diprotonated ligand.

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

In recent years, there has been an increase of research in coordination chemistry with molybdenum, especially the molybdenum(VI) complexes due to their facile preparations, structure flexibilities and high stabilities.[17] Moreover, this growing interest is due to the similarity between the studied Mo(VI) complexes and the active sites in most of molybdo-enzymes,[1] leading to interesting properties, for example antiviral and antibacterial activities.[19]

In addition to their numerous biological activities, Mo(VI) complexes also show high efficiency in oxygen atom transfer reactions with a wide range of substrates, including epoxidation of olefins as well as oxidation of saturated hydrocarbons, alcohols and sulfides.[17]

This thesis will concern dioxomolybdenum(VI) complexes with *ONO* type of hydrazone ligand since they have been intensively investigated as oxidation catalysts for the already mentioned reactions of olefin epoxidations.[4,7]

Molybdenum(VI) complexes are usually prepared by the reaction of [$MoO_2(acac)_2$] or [MoO_2Cl_2] with corresponding hydrazone ligand in methanol, ethanol or acetonitrile. These complexes consist of a *cis*-$\{MoO_2\}^{2+}$ core and a tridentate *ONO* donor ligand coordinated through phenolate-oxygen, imino-nitrogen and enolate-oxygen. In general, there are three types of dioxomolybdenum(VI) complexes with *ONO* type of hydrazone ligand (Figure 4). Mononuclear complexes [MoO_2(L)(D)], where L^{2-} is corresponding ligand and D is donor molecule, dinuclear [MoO_2(L)]$_2$ and polynuclear one [MoO_2(L)]$_n$. Coordination around molybdenum is distorted octahedral. In the case of mononuclear complexes, sixth coordination site is occupied by the donor molecule (D), but in polynuclear and dinuclear complexes it can be occupied by the oxygen atom from a Mo=O unit of the neighbouring molecule or by another donor atom present on the ligand. This donor atom is in most cases N or O.[4,6,14]

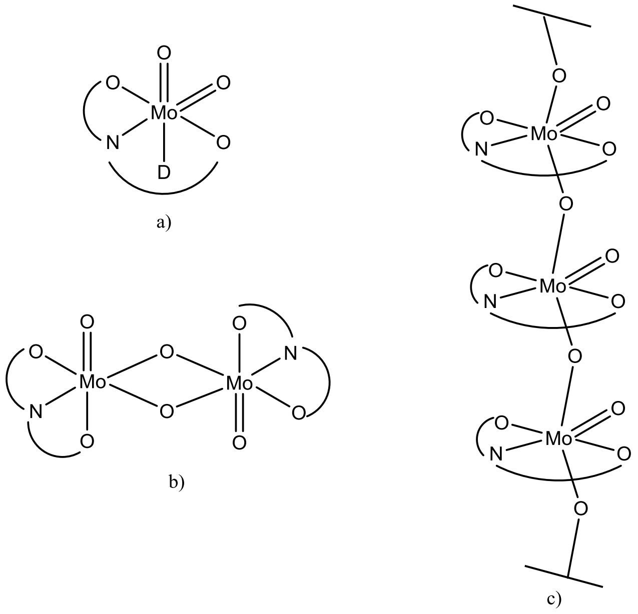


Figure 4. General types of dioxomolybdenum(VI) complexes with *ONO* donor ligand:
a) mononuclear, b) dinuclear, c) polynuclear.

In the reaction of [$MoO_2(acac)_2$] in ethanol with hydrazone ligands 3-methoxysalicylaldehyde 4-hydroxybenzhydrazone (H_2L^{3OMe}), 4-methoxysalicylaldehyde 4-hydroxybenzhydrazone (H_2L^{4OMe}) or salicylaldehyde 4-hydroxybenzhydrazone (H_2L^{H}), mononuclear molybdenum(VI) complexes were obtained (Figure 5).[9] In all three complexes, sixth coordination site is occupied by ethanol molecule.

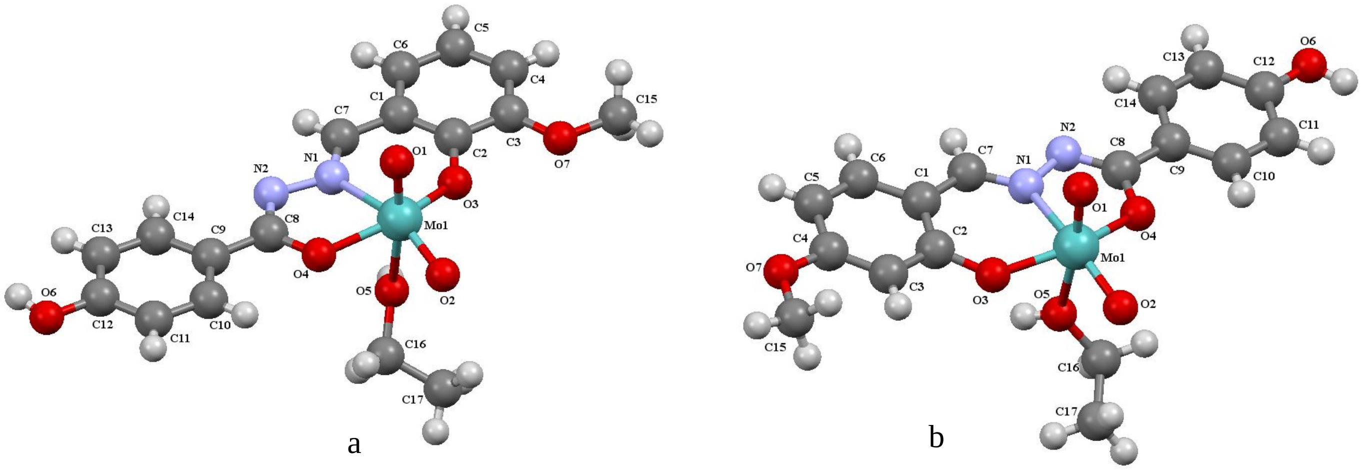


Figure 5. Structure of mononuclear molybdenum(VI) complexes:
a) $[MoO_2(L^{3OMe})(EtOH)]$ and b) $[MoO_2(L^{4OMe})(EtOH)]$.[9]

The IR spectra of mononuclear complexes showed vibrations characteristic for the $\{MoO_2\}$ core at 935 cm^{-1} and $O{=}Mo{-}O_{EtOH}$ stretching at 910 cm^{-1} and 890 cm^{-1}.

Heating of the mononuclear complexes in acetonitrile or dichloromethane resulted in the formation of polynuclear structures ($[MoO_2(L^R)]_n$) (Figure 6). After the loss of the solvent molecule (EtOH) on the sixth coordination site, the oxygen atom of the $\{MoO_2\}^{2+}$ core interacted with the Mo atom of the neighbouring molecule. The IR spectra showed a strong vibration at 850 cm^{-1} due to polymerisation through $Mo{=}O{-}Mo$ bonding.

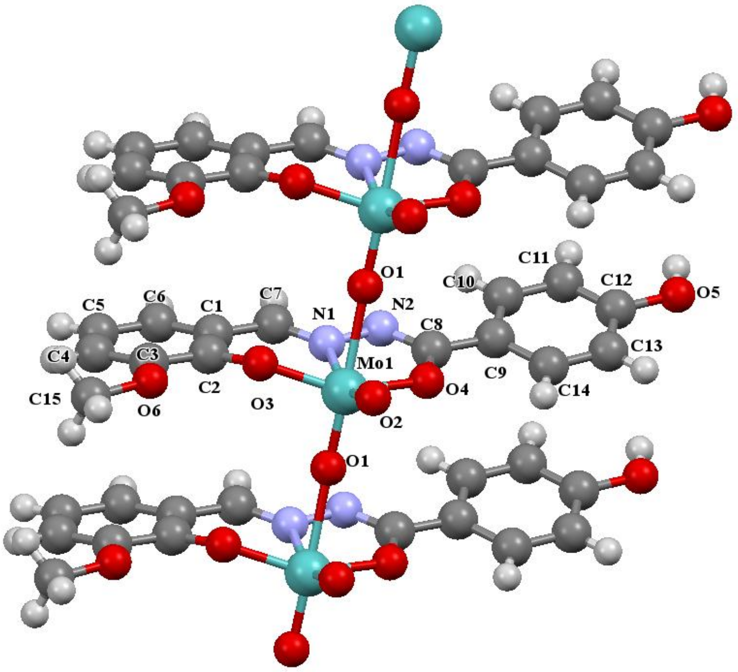


Figure 6. Molecular structure of polynuclear $[MoO_2(L^{3OMe})]_n$ complex.[9]

When the reaction was carried out solvothermally, in dry dichloromethane, a dark red dinuclear $[MoO_2(L^{3OMe})]_2$ was obtained (Figure 7).[9] In the IR spectra strong stretching frequency was observed at 833 cm^{-1}, which is characteristic for the Mo_2O_2 core.

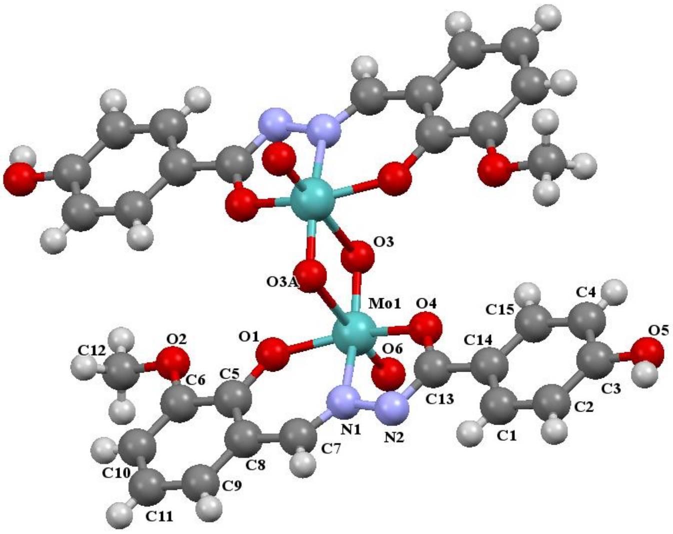


Figure 7. Molecular structure of dinuclear $[MoO_2(L^{3OMe})]_2$ complex.[9]

As mentioned before, in polynuclear and dinuclear complexes, the sixth coordination site of molybdenum(VI) complexes with *ONO* donor ligands, can be occupied by another donor group present on the ligand and this donor group is in most cases the NH_2 group. The reaction of $[MoO_2(acac)_2]$ with 4-aminobenzoylhydrazone based ligands yielded mononuclear and dinuclear molybdenum(VI) complexes.[4] The mononuclear complexes were obtained when the reaction was carried out in a methanol or ethanol solutions (Figure 8).

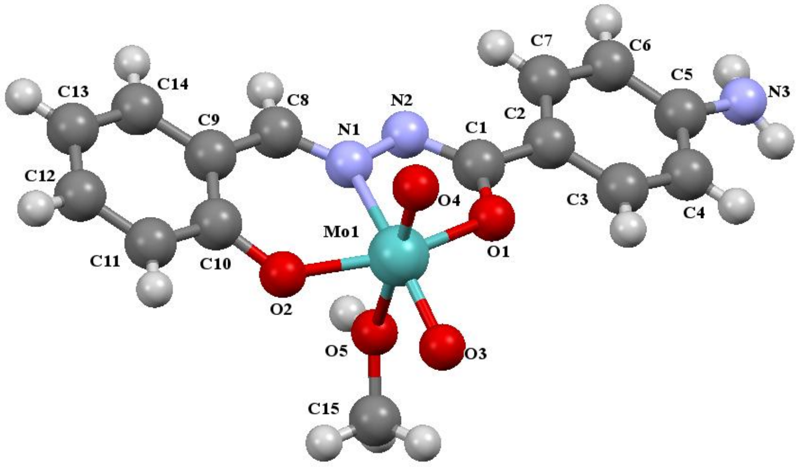


Figure 8. Structure of mononuclear complex $[MoO_2(L)(MeOH)]$ where L=salicylaldehyde 4-aminobenzoylhydrazone.[4]

A distorted octahedron, with MoO_2^{2+} and tridentate 4-aminobenzoylhydrazone ligand, is completed by the oxygen atom from the coordinating solvent, in this case methanol. The IR spectra of all complexes showed vibrations in regions 930-944 cm^{-1} which corresponds to $\upsilon_{asym}(MoO_2)$ and bands at 917-933 cm^{-1} for $\upsilon_{sym}(MoO_2)$. Furthermore, for mononuclear complexes obtained from methanol solution, vibration observed in region from 897 cm^{-1} to 909 cm^{-1} (depends which ligand is coordinated) is characteristic for $O{=}Mo{-}O_{MeOH}$ stretching.

As for the dinuclear complexes, the synthesis required the absence of strongly donating solvents like methanol or ethanol. They were obtained from the reaction of $[MoO_2(acac)_2]$ with tridentate 4-aminobenzoylhydrazone ligand in dry acetonitrile. In dinuclear complexes sixth coordination site is occupied by amino nitrogen atom acting as donor (Figure 9).[4] The $N{-}H_{amino}$

stretching frequency observed in the IR spectra shifted by 120 cm^{-1} in comparison with the spectra of mononuclear complex.

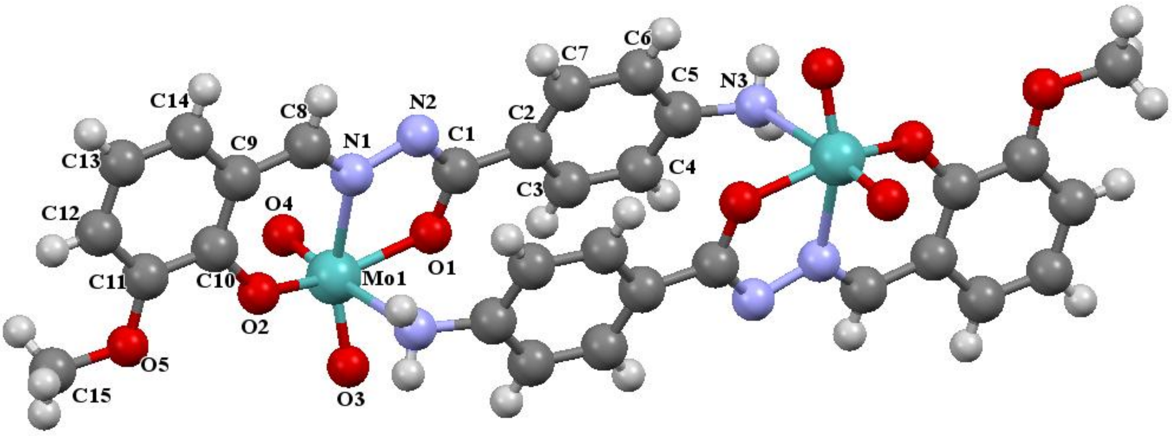


Figure 9. Structure of dinuclear complex [MoO$_2$(L)]$_2$ where L=3-methoxysalicylaldehyde 4-aminobenzoylhydrazone.[4]

In all complexes the bands characteristic of the N–H and C=O groups (at 3150 cm^{-1} and 1645 cm^{-1}) are absent and that suggest tautomerism involving hydrazone forms (=N–NH–(C=O)– ⇔ =N–N=(C–OH)–), deprotonation and coordination of tridentate *ONO* ligand through oxygen atom is present.

2.3. Epoxidation of olefins catalyzed by molybdenum(VI) complexes

2.3.1. Green chemistry and catalysis

The need for environmentally friendly chemical processes in the industry is increasing. That trend is now known as Green Chemistry concept and it refers to the environmental impact of the chemical processes and products. The definition of green chemistry has been written as follows : "*Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products."*[8] The concept of Green Chemistry has been summarized within twelve rules. Some useful measurements (called "Green metrics") of the potential environmental acceptability of chemical processes have been also defined. One of those measurements is the E factor.[8] E factor is defined as the mass ratio of waste to the desired product. It takes all that can consider as waste but water. Higher E factor means more waste and greater negative impact on environment. Another useful measurement is atom efficiency which is defined as ratio of molecular weight of the desired product and sum of the molecular weights of all substances produced in the stoichiometric equation.[8]

The great need for green chemistry and green catalytic substances is high in oxidation reactions. Indeed, chromium(VI) reagents, permanganate, manganese dioxide are still in great use although they are quite toxic and polluting, and there is a need for clean primary oxidants such as oxygen and hydrogen peroxide.[8]

Important parameters describing the efficiency of catalytic reactions are conversion ($\mathrm{CON_R}$), selectivity (S), turnover number (TON) and turnover frequency (TOF).

If the catalysed reaction schemes as followed:

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

where a reactant (R) gives a product (P) and by-product (Q) using a catalyst (cat).

The conversion of a reactant R is defined as the ratio of the amount of consumed reactant $n_{\mathrm{R}(t)}$ (at considered reaction time t) and its initial amount $n_{\mathrm{R}(0)}$ (at $t = 0$) (equation 1).

$$\mathrm{CON_R} = \frac{n_{\mathrm{R\ consumed}}}{n_{\mathrm{R}(0)}} \times 100\ (\%) = \frac{n_{\mathrm{R}(0)} - n_{\mathrm{R}(t)}}{n_{\mathrm{R}(0)}} \times 100\ (\%) \quad (1)$$

The selectivity (S) is expressed as the molar ratio of desired product P formed $n_{\mathrm{P}(t)}$ and the reactant consumed $n_{\mathrm{R\ consumed}}$ at a time t (equation 2), where $n_{\mathrm{R\ consumed}}$ at a time t is expressed as difference of $n_{\mathrm{R}(t)}$ (at considered reaction time t) and its initial amount $n_{\mathrm{R}(0)}$ (at $t = 0$).

$$\mathrm{S_P} = \frac{n_{\mathrm{P}(t)}}{n_{\mathrm{R\ consumed}}} \times 100\ (\%) = \frac{n_{\mathrm{P}(t)}}{n_{\mathrm{R}(0)} - n_{\mathrm{R}(t)}} \times 100\ (\%) \quad (2)$$

TON (Turn Over Number) is the number of catalytic cycles that a catalyst can achieve, *i.e*. the number of molecules of reactant converted with one molecule of the catalyst. The value of TON is usually calculated at the end of a reaction. TON is mathematically expressed as the ratio of product P produced up to the time t and amount of catalyst used in the reaction (equation 3). Product P is expressed as $n_{\mathrm{R\ consumed}}$, where $n_{\mathrm{R\ consumed}}$ at a time t is expressed as difference of $n_{\mathrm{R}(t)}$ (at considered reaction time t) and its initial amount $n_{\mathrm{R}(0)}$ (at $t = 0$).

$$\mathrm{TON} = \frac{n_{\mathrm{R\ consumed}}}{n_{\mathrm{catalyst}}} = \frac{n_{\mathrm{R}(0)} - n_{\mathrm{R}(t)}}{n_{\mathrm{catalyst}}} \quad (3)$$

TOF (Turn Over Frequency) is the value that defines the activity of a catalyst at specific time intervals, the number of molecules of reactant consumed per time unit. It is the ratio of reactant R transformed in a time interval Δt (between t_{x} and $t_{\mathrm{x+1}}$) and the amount of catalyst used in reaction, all divided by the time interval (equation 4).

$$\mathrm{TOF} = \frac{n_{\mathrm{R\ consumed\ in\ }\Delta t}}{n_{\mathrm{catalyst}}} \times \frac{1}{\Delta t} = \frac{n_{\mathrm{R}(t_{\mathrm{x}})} - n_{\mathrm{R}(t_{\mathrm{x+1}})}}{n_{\mathrm{catalyst}}} \times \frac{1}{t_{\mathrm{x+1}} - t_{\mathrm{x}}} \ \left(time^{-1}\right) \quad (4)$$

2.3.2. Organic solvent-free epoxidation

Epoxidation of olefins is an important reaction in organic synthesis since epoxides are very important in the chemical industry. Epoxides are raw materials for the synthesis of other chemicals such as alcohols, carbonyl compounds, polymers like polyesters and epoxy resins.[2] Because of the great use of epoxides in industry, the development of catalysts promoting oxygen transfer is important.

Metal-catalysed oxidation reactions converting olefins to epoxides usually proceed by the oxygen atom transfer reaction using oxidants such as *tert*-butyl hydroperoxide, O_2 or hydrogen peroxide, in organic solvents. With an increasing need for environmentally friendly or greener chemical processes, it is desirable to replace or to suppress organic solvents within the process.[9] Organic solvent-free epoxidation of olefins includes oxidation with alkyl hydroperoxide or hydrogen peroxide catalysed by metal complexes.

For the epoxidation of olefins, progress has been achieved towards greener methods by using homogenous metal complexes.[8]

2.3.3. Molybdenum(VI) complexes as catalysts

Cyclooctene is widely applied as model substrate for olefin epoxidation reactions. The product of those reactions is the corresponding epoxide, usually providing high selectivity. When using a least reactive olefin as substrate, *e.g.* oct-1-ene, differences in the activity of Mo(VI) complexes as epoxidation catalysts can be better pronounced, exhibiting the low reactivity towards epoxidation of linear alkenes.[21]

A wide variety of molybdenum(VI) complexes with tridentate *ONO* ligands have high catalytic activity and selectivity in cyclooctene epoxidation. The catalytic activity of Mo(VI) complexes correlates with the possibility of the complex to be converted into the pentacoordinated intermediate.[4] Conversion of complex to pentacoordinated species [MoO_2L], where L is a tridentate ligand, is promoted when complex is more soluble.[4] The formed pentacoordinated dioxomolybdenum species have a great tendency to form polymeric structures, dimeric or monomeric structures, depending on the solvent used. The catalytic activity of Mo(VI) complexes varies with the different types of ligands and coordination sites.[2]

The catalytic activity of the mononuclear and dinuclear complexes with tridentate 4-aminobenzoylhydrazone and 2-aminobenzoylhydrazone ligands was investigated in solvent-free epoxidation reactions of cyclooctene. In reaction, no solvent was added following green chemistry conditions and TBHP as 70 % aqueous solution was used as an oxidizing agent.[4,14] General mechanism for olefin epoxidation was proposed (Figure 10).[22]

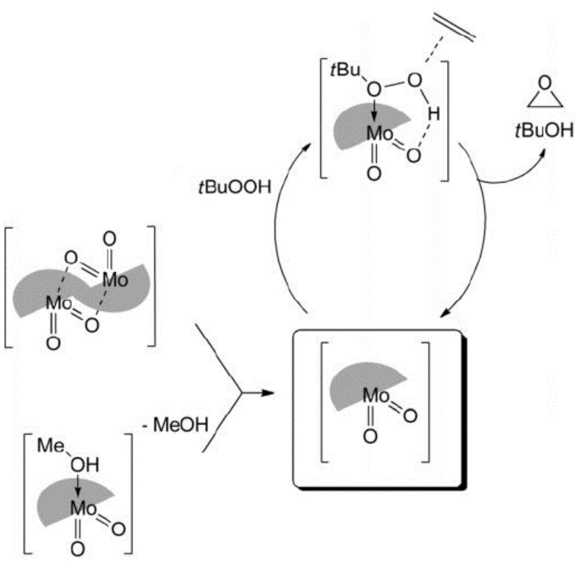


Figure 10. Proposed mechanism for the catalytic epoxidation of olefins by Mo(VI) complexes and TBHP as oxidant.[22]

Pentacoordinated [MoO$_2$L] species is formed by dissociation of coordinated alcohol, in case of mononuclear complex, or by dimer splitting in case of dimer structure. After the formation of pentacoordinated species, one neutral molecule of TBHP occupies the sixth coordination site forming a [MoO$_2$(L)(*t*-BuOOH)] adduct complex. The metal centre withdraws electrons from O–O bond of coordinated peroxide which makes it more approachable for nucleophilic olefin attack.[8]

In epoxidation of cyclooctene where ligand was of 4-aminobenzoylhydrazone nature, the dinuclear complexes show a wider range of catalytic activity than mononuclear ones.[4] For mononuclear complexes conversion ranges from 47 % to 63 %, and for the dinuclear complexes conversion values range from 38 % to 89 %. Because of the weak donor properties of the coordinated amino group, formation of pentacoordinated [MoO$_2$L] species is easier and dinuclear complexes show better conversion values than mononuclear ones.[4]

As for the reaction with Mo(VI) complexes with 2-aminobenzoylhydrazone ligands all complexes reach conversion values between 84 and 89 %.[14]

The position of the amino group on phenyl ring influences catalytic activity of the Mo(VI) complexes. Comparing the results, 2-aminobenzoylhydrazone derived complexes transform more easily to the pentacoordinated species than those containing 4-aminobenzoylhydrazone ligands, and therefore catalytic activity and conversion values are higher.[14]

§ 3. EXPERIMENTAL SECTION

Solvents and starting reagents (Aldrich) were commercially available and used without previous purification. For catalytic reactions, molar concentrations of used oxidants were: aqueous TBHP, 7.76 M; TBHP in decane, 5.5 M, H_2O_2, 10.29 M.

Infrared spectra were recorded with Perkin-Elmer 502 spectrophotometer in the region of 4000–400 cm^{-1}, using Attenuated Total Reflectance technique (ATR). All data were processed in Omnic and SpectraGryph programme.

Thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA851 thermobalance using aluminium crucibles, in an oxygen atmosphere and temperature range from 25 to 600 °C, with a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) analyses were performed in a nitrogen atmosphere and temperature range from 25 to 400 °C, with heating rate of 10 °C min^{-1}.

The powder X-ray diffraction data were collected by the Panalytical X’Change powder diffractometer in the Brag-Brentano geometry using Cu-K_α radiation. Patterns were collected in the range of 2θ = 5–50° with a step size of 0.03° and 1.5 s per step. All data were collected and visualized using X’pert programs suite.

Chromatograms were obtained using Agilent 7820A chromatograph with FID detector and HP5-MS capillary column (30 m × 0.32 mm × 0.25 μm). The GC parameters were quantified with authentic samples of the reactants and products. After the injection of sample, it is exposed to a temperature of 50 °C for 5 minutes, after which it is heated to 220 °C at a rate of 10 °C/min. Heater: 270 °C, H_2 flow 30 mL/min, air flow 280 mL/min. Conversion of olefins and formation of corresponding epoxides were calculated from calibration curves relative to acetophenone as an internal standard.

Liquid assisted grinding (LAG) experiments were performed using a Retsch MM200 ball mill.

For complexes identification, 1D (1H, ^{13}C-DEPTq) and 2D (COSY, HSQC, HMBC) solution NMR spectra were recorded on Bruker Avance III HD 400 MHz/54 mm Ascend spectrometer equipped with a 5 mm PA BBI 1H/D-BB Z-GRAD probe head. All measurements were performed at 298 K using standard Bruker pulse programs. DMSO-d^6 was used as solvent and TMS as internal standard for proton and carbon chemical shifts.

3.1. Preparation of starting compounds

3.1.1. Dioxobis(pentane-2,4-dionato)molybdenum(VI), [$MoO_2(acac)_2$][23]

4 mL (2.4 mmol) of acetylacetone, $C_5H_8O_2$, was added to the aqueous solution of ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\times 4H_2O$, 3 g (0.04 mmol) in 15 mL. A pH value of the solution was adjusted to 3.5 with the 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.[23] Yield: 1.73 g (32.9 %).

3.1.2. Ligands 2-amino-(2,3-dihydroxybenzylidene)benzohydrazide, (H_2L^1) and 4-amino-(2,3-dihydroxybenzylidene)benzohydrazide, (H_2L^2)

General procedure: Solution based synthesis. 1.1 g (7.23 mmol) of an appropriate aminobenzhydrazide was dissolved in 50 mL of methanol and 1.0 g (7.24 mmol) of an appropriate dihydroxybenzaldehyde was added and stirred. The dark orange solution was refluxed for two more hours.

*3.1.2.1. 2-amino-(2,3-dihydroxybenzylidene)benzohydrazide, (**H_2L^1**)*

The obtained light yellow product was filtered off after two days. Yield: 0.31 g (15.9 %). Selected IR data (cm^{-1}): 3460, 3338 (O-H), 3160, 3114 (NH_2), 1627 (C=O), 1616 (C=N). DSC onset at 196 °C, $E= -29\ 057.44$ J/mol

*3.1.2.2. 4-amino-(2,3-dihydroxybenzylidene)benzohydrazide, (**H_2L^2**)*

The obtained light orange product was filtered off. Yield: 1.63 g (82.9 %). Selected IR data (cm^{-1}): 3413, 3341 (O-H), 3259, 3230 (NH_2), 1646 (C=O), 1603 (C=N). DSC onset at 273 °C, $E= -43\ 615.99$ J/mol

General procedure: Mechanochemical synthesis. 0.15 g (0.1 mmol) of an appropriate dihydroxybenzaldehyde and 0.164 g (0.1 mmol) of an appropriate aminobenzhydrazide was mixed in teflon jar and 50 μL of methanol was added. The reaction mixture was milled for 60 minutes at a frequency of 25 Hz.

3.2. Synthesis of molybdenum(VI) complexes

3.2.1. Dinuclear complexes [MoO$_2$(L)]$_2$

General procedure: 0.083 g (0.306 mmol) of the H_2L^1 or H_2L^2 ligand was dissolved in 50 mL of acetonitrile and 0.1 g (0.307 mmol) of [MoO$_2$(acac)$_2$] was added. The orange reaction mixture was refluxed for 3 hours at 50-60 °C. The obtained product was filtered off.

*3.2.1.1. [MoO$_2$(L^1)]$_2$, complex **1***

Yellow product. Yield: 0.104 g (86.1 %). Mass fraction of elements, *w* / %, calculated (experimental), for $C_{28}H_{22}Mo_2N_6O_{10}$, are: C, 43.13 (42.13); H, 3.02 (2.58); N, 11.74 (11.02). Selected IR data (cm^{-1}): 3251, 3214 (NH$_2$), 1614 (C=N$_{\text{imine}}$), 1591 (C=C), 1341 (C–O), 1263 (C–O$_{\text{phenolate}}$), 921, 906 (MoO_2^{2+}), 895 (Mo–N). TG: calcd. for MoO$_3$, 36.24 %, found 37.41 %. ^{1}H NMR (δ/ppm): Ha (8.93, s), Hb (7.09, dd), Hc (6.93, t), Hd (9.41, s), He (7.12, dd), Hf (7.21, ddd), Hg (6.80, dd), Hh (7.69, dd), Hi (6.58, ddd), Hj (7.00, s), Hk (7.00, s); ^{13}C NMR (δ/ppm): C1 (155.5), C2 (121.2), C3 (121.1), C4 (122.1), C5 (124.5), C6 (169.9), C7 (148.3), C8 (149.9), C9 (109.4), C10 (133), C11 (116.5), C12 (130.4), C13 (115.3), C14 (146.7) (Supplement, Figure D27).

*3.2.1.2. [MoO$_2$(L^2)]$_2$ × MeCN, complex **2×MeCN***

Yellow-orange product. Yield: 0.1064 g (87.8 %). Mass fraction of elements, *w* / %, calculated (experimental) for $C_{30}H_{25}Mo_2N_7O_{10}$, are: C, 42.33 (41.89); H, 2.79 (1.84); N, 10.58 (9.85). Selected IR data (cm^{-1}): 3331 (NH$_2$), 1602 (C=N$_{\text{imine}}$), 1568 (C=C), 1326 (C–O), 1255 (C–O$_{\text{phenolate}}$), 919, 910 (MoO_2^{2+}), 879 (Mo–N). TG: calcd. for MoO$_3$, 34.47 %, found 37.25 %, for MeCN calcd. 4.91 %, found 4.98%. ^{1}H NMR (δ/ppm): Ha (8.72, s), Hb (7.02, dd), Hc (6.85, t), Hd (9.35, s), He (7.12, dd), Hf (7.65, m), Hg (6.60, m), Hh (6.60, m), Hi (7.65, m), Hj (5.92, s), Hk (5.92, s) ^{13}C NMR (δ/ppm): C1 (153.7), C2 (121.5), C3 (120.6), C4 (121.9), C5 (124.2), C6 (169.8), C7 (148.2), C8 (153.1), C9 (116.3), C10 (130.3), C11 (113.6), C12 (146.6), C13 (113.6), C14 (130.3) (Supplement, Figure D28).

3.2.1.3. $[MoO_2(L^2)]_2$, complex ***2***

Complex 2 was obtained after the heating of complex **2xMeCN** at 120 °C for two hours. Orange product. Mass fraction of elements, *w* / %, calculated (experimental) for $C_{28}H_{22}Mo_2N_6O_{10}$, are: C, 42.33 (41.45); H, 2.79 (2.03); N, 10.58 (9.14). TG: calcd. for MoO_3, 36.24 %, found 37.92 %.

3.2.2. Mononuclear complexes $[MoO_2(L)(MeOH)]$

General procedure: 0.083 g (0.306 mmol) of the H_2L^1 or H_2L^2 ligand was dissolved in 50 mL of methanol and refluxed for 1 hour after which 0.1 g (0.307 mmol) of $[MoO_2(acac)_2]$ was added. The yellow reaction mixture was cooled to room temperature and then stored at -8 °C for one month. The obtained products were filtered off.

3.2.2.1. $[MoO_2(L^1)(MeOH)]$, complex ***1a***

Yellow product. Yield: 0.015 g (12.8 %). Mass fraction of elements, *w* / %, calculated (experimental) for $C_{15}H_{15}MoN_3O_6$, are: C, 41.97 (40.38); H, 3.52 (3.12); N, 9.79 (9.18). Selected IR data (cm^{-1}): 3331, 3256 (NH_2), 1613 ($C{=}N_{imine}$), 1574 (C=C), 1327 (C–O), 1240 ($C–O_{phenolate}$), 916 (MoO_2^{2+}), 893 ($Mo–O_{MeOH}$). TG: calcd. for MoO_3, 33.54 %, found 33.54 %, for MeOH calcd. 7.46 %, found 7.46 %.

3.2.2.2. $[MoO_2(L^2)(MeOH)]$, complex ***2a***

Brown product. Yield: 0.075 g (61.5 %). Mass fraction of elements, *w* / %, calculated (experimental) for $C_{15}H_{15}MoN_3O_6$, are: C, 41.97 (40.89); H, 3.52 (2.78); N, 9.79 (8.15). Selected IR data (cm^{-1}): 3426 (NH_2), 1602 ($C{=}N_{imine}$), 1568 (C=C), 1347 (C–O), 1261 ($C–O_{phenolate}$), 938, 919 (MoO_2^{2+}), 891 ($Mo–O_{MeOH}$). TG: calcd. for MoO_3, 33.54 %, found 33.33 %, for MeOH calcd. 7.46 %, found 12.97 %.

3.3. General procedure for the epoxidation of olefins

20 mmol of olefin (2.204 g of *cis*-cyclooctene or 2.244 g of oct-1-ene) and □ 0.1 g of acetophenone were stirred together. 0.05 mol% of Mo(VI) (pre)catalyst was added in the mixture *i.e.* 0.05 mmol of the polynuclear and mononuclear complex. The mixture was stirred

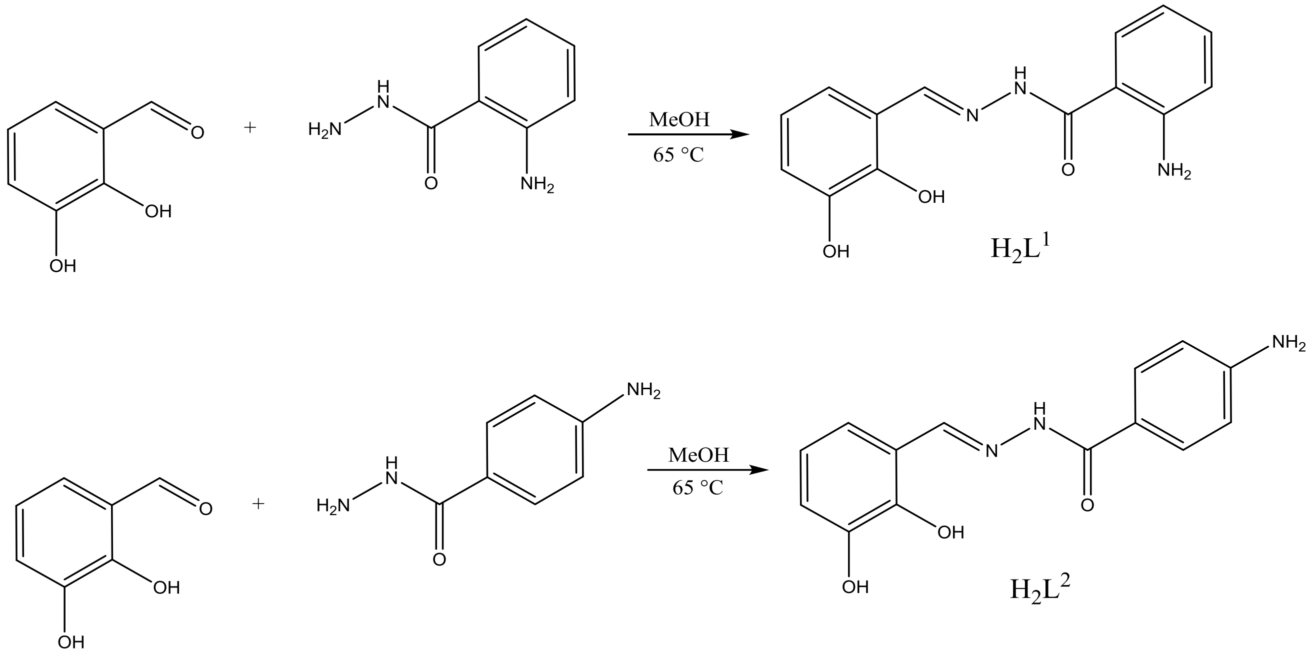
and heated up to 80 °C before adding 40 mmol of oxidant (5.48 mL of aqueous TBHP or 3.48 mL of H_2O_2 or 7.27 mL of TBHP in decane).

All reactions were monitored for 5 hours. At defined times 0, 20, 50, 90, 150, 300 minutes, aliquots (≈0.1 mL) of the organic phase were taken from the reaction mixture and diluted with Et_2O. Catalytic reactions were followed along the time through GC measurements. In the reaction in which TBHP in decane was used as the oxidant, defined times for taking aliquots for the analysis were 0, 2.5, 5, 10, 15, 20, 30 minutes.

§ 4. RESULTS AND DISCUSSION

4.1. Aminohydrazone ligands

The hydrazone ligands were prepared by the reaction of 2,3-dihydroxybenzaldehyde and corresponding hydrazide (2-amino or 4-aminobenzhydrazide), 1:1, in the refluxing methanol solution (Scheme 2). H_2L^1 ligand was obtained in low yield (17.4 %) whereas H_2L^2 ligand in high yield (82.9 %).



Scheme 2. Synthesis of hydrazones.

Both ligands exhibit two bands in range of 3338 cm^{-1} to 3460 cm^{-1} assigned to O–H stretching and two bonds in range of 3114 cm^{-1} to 3259 cm^{-1} assigned to N–H bond vibrations. Also, in the range of 1603 – 1616 cm^{-1} absorption band is present which is characteristic for C=N$_{\text{imine}}$ bond stretching. Bands present in range of 1627 cm^{-1} to 1646 cm^{-1} correspond to C=O bond stretching. Selected stretching vibrations of obtained ligands are summarized in Table 1.

Table 1. Selected stretching vibrations of hydrazone ligands.

	Selected IR data (cm^{-1})	
	H_2L^1	H_2L^2
O-H	3460	3413
	3338	3341
N-H	3160	3259
	3114	3230
C=O	1627	1646
C=N	1616	1603

Due to the fact that large amount of methanol was used for the ligand preparation (50 ml per synthesis), the idea was to diminish the solvent in order to follow principles of green chemistry. A solution to this problem is mechanochemistry, as a branch of chemistry that eliminates the need for larger quantities of solvents and can make many chemical processes environmentally friendly. Mechanochemical synthesis of ligands was followed by powder X-ray diffraction. A sample of the powder was taken at different reaction times within one hour and subjected to PXRD qualitative analysis. Figure 11 shows a gradual formation of the ligand and a comparison of the collected data with the powder patter calculated from the previously determined crystal structure of monocrystalline sample.

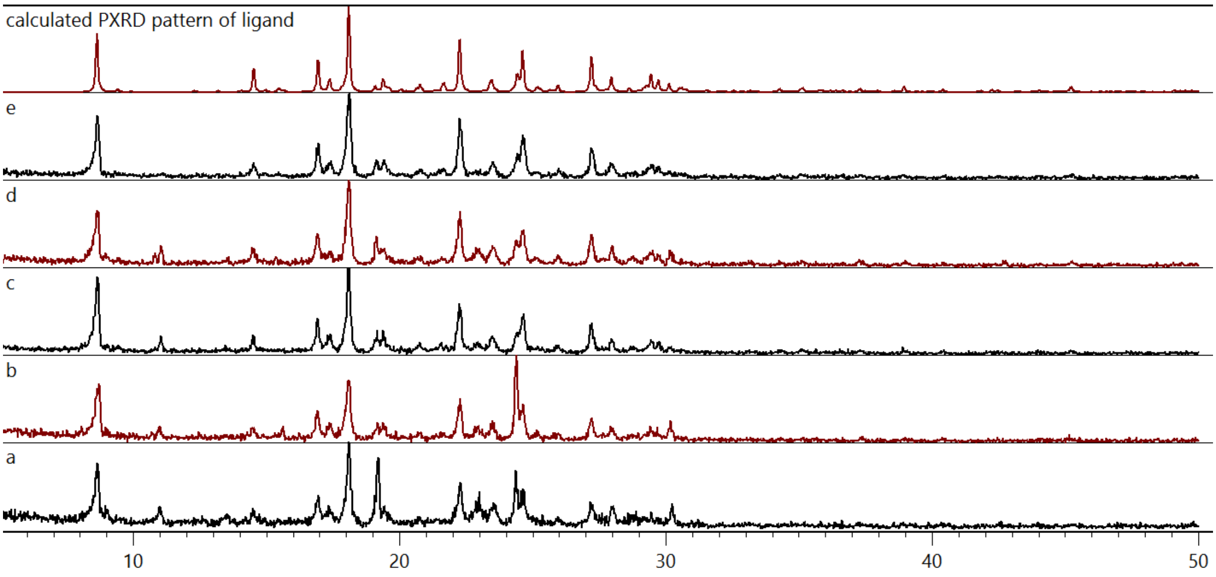


Figure 11. Comparison of the obtained PXRD patterns of samples taken at 10 min (a), 20 min (b), 30 min (c), 40 min (d), 60 min (e) of mechanochemical reaction with calculated PXRD pattern of H_2L^2 ligand.

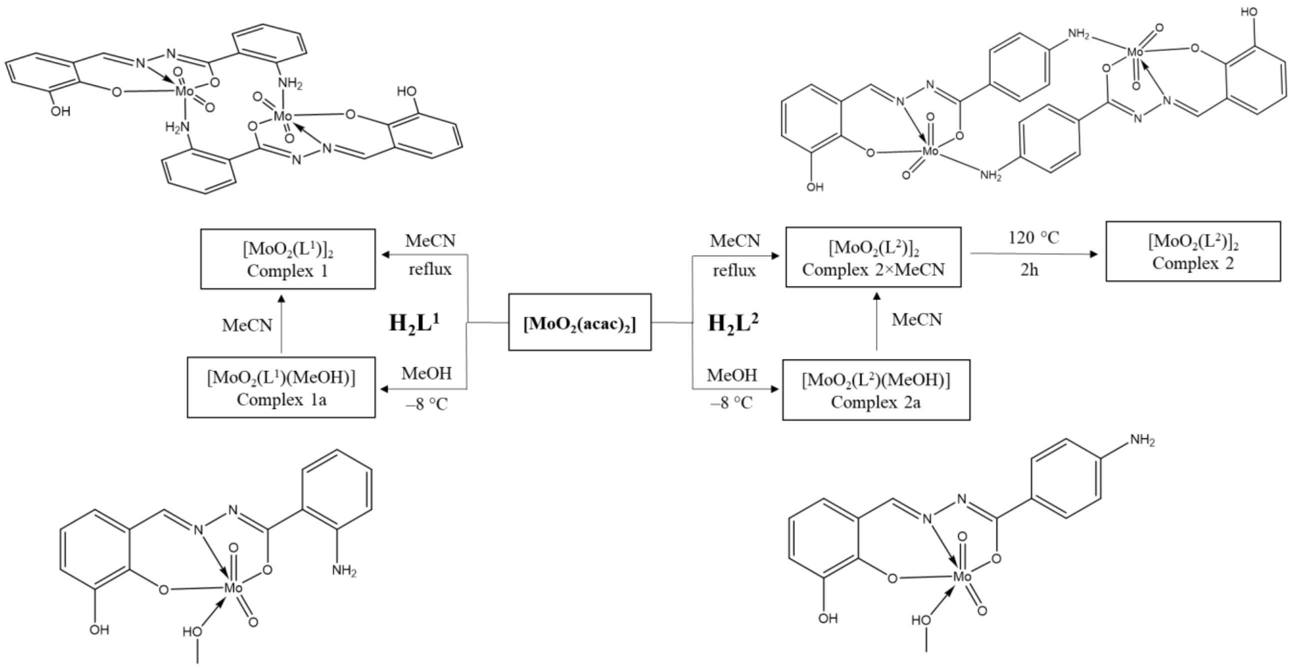
DSC analysis of the obtained ligands showed sharp endothermic minimum attributed to the melting point, onset at 196 °C, $E = -29\ 057.44$ J/mol for $\mathbf{H_2L^1}$ and onset at 273 °C, $E = -43\ 615.99$ J/mol for $\mathbf{H_2L^2}$.

4.2. Dioxomolybdenum(VI) complexes: synthesis and characterization

The reaction of equimolar amounts of $[MoO_2(acac)_2]$ and corresponding aminobenzhydrazone ligand (H_2L^1 or H_2L^2) in methanol or acetonitrile resulted in the formation of four different complexes. Despite many attempts, good quality crystals of any of the products for single-crystal X-ray diffraction experiments were not obtained.

Two dinuclear products, yellow $[MoO_2(L^1)]_2$ (**1**) and dark orange $[MoO_2(L^2)]_2$×MeCN (**2×MeCN**), were obtained from acetonitrile while mononuclear complexes, yellow $[MoO_2(L^1)(MeOH)]$ (**1a**) and brown $[MoO_2(L^2)(MeOH)]$ (**2a**), were obtained from methanol solutions. (Scheme 3). The process of crystallization for mononuclear complex **1a** lasted for at least one month and the product was obtained in very low yield relative to the other three complexes (12.8 % in comparison with 86.1 % for **1**, 87.8 % for **2×MeCN**, 61.5 % for **2a**).

Recrystalization of synthesized mononuclear complexes **1a** and **2a** in acetonitrile resulted in the formation of dinuclear complexes **1** and **2×MeCN**. Furthermore, by exposing complex **2** (dried **2×MeCN**) to the acetonitrile vapours, molecule of acetonitrile is incorporated into the crystal structure and **2×MeCN** is obtained. These feature is very interesting since it gives an opportunity to use the complex as acetonitrile sensor.



Scheme 3. Dinuclear and mononuclear molybdenum(VI) complexes.

In all complexes, bands around 3481 cm^{-1}, 3413 cm^{-1} are assigned to O–H stretching and around 3114 cm^{-1}, 3259 cm^{-1} to N–H bond vibrations. Also, vibration in the range of 1614 – 1602 cm^{-1} is characteristic for C=N$_{\text{imine}}$ bond stretching. C–O$_{\text{phenolic}}$ absorption bands are in the range of 1240 – 1263 cm^{-1}. Absence of vibrations, characteristic for C=O group around 1650 cm^{-1}, indicates tautomerization of ligands and coordination through the deprotonated oxygen atom.

For all the complexes, strong vibrations in the range 910 – 938 cm^{-1} are characteristic for $\{MoO_2\}^{2+}$ core. For dinuclear structures absorption bands in the range of 879 – 895 cm^{-1} confirm that the coordination sphere of molybdenum is completed by the nitrogen atom from the neighbouring complex molecule. By the absence of a strong band at around 800 cm^{-1}, which is characteristic for intermolecular Mo=O$_t$···Mo interaction, the latter claim was confirmed to be correct. In mononuclear structures absorption band at 1010 cm^{-1} and 1017 cm^{-1} indicates the presence of coordinated MeOH, typical band for MeOH is around 1022 cm^{-1}. It can be concluded that in mononuclear structures **1a** and **2a**, the sixth coordination site of central molybdenum atom, is occupied with the methanol molecule. For dinuclear complexes **1** and **2**, dimerization occurred through N atom of the amino group from the neighboring ligand. For the complex **2×MeCN**, absorption maximum characteristic for MeCN was not seen in IR spectra. Presence of the MeCN molecule was later confirmed by TG analysis.

Selected stretching vibrations of molybdenum(VI) complexes are summarized in Table 2 and IR spectra of ligands and complexes are shown in the Supplement (Figure D1-8).

Table 2. Selected stretching vibrations of molybdenum(VI) complexes.

	Selected IR data (cm^{-1})			
	Mo–N	C=N	C–O$_{hydrazonic}$	C–O$_{phenolic}$
1	895	1614	1342	1263
2×MeCN	879	1602	1325	1255
	Mo–O$_{MeOH}$	C=N	C–O$_{hydrazonic}$	C–O$_{phenolic}$
1a	893	1613	1327	1240
2a	878	1602	1347	1261

Comparing the results with previously published experimental data of molybdenum(VI) complexes with aminohydrazones as ligands, it can be observed that the wavenumber values are quite close.[4,14] For example, in complexes **1** and **1a** C=N band is present at 1614 cm^{-1} (1613 cm^{-1}) while those values are the same in different complexes with similar ligand coordinated to Mo centre.[14] Wavenumbers values of MoO_2^{2+} core are slightly different in complexes **2×MeCN** and **2a** and values from literature, 919, 910 cm^{-1} in comparison with 914, 906 cm^{-1}.

All complexes were analysed by thermogravimetry under oxygen atmosphere and in a temperature range from 25 to 600 °C. As a product of thermal decomposition molybdenum(VI) oxide, MoO_3, was formed (which was confirmed by comparison of the PXRD spectra obtained from TG residue and commercially available MoO_3). The results of the thermogravimetric analysis are shown in Table 3.

Table 3. Results of thermogravimetric analysis.

	w_{exp} / % (w_{theor} / %)		
	MoO_3	MeOH	MeCN
1	37.37 (36.24)	-	-
2×MeCN	37.28 (34.47)	-	4.98 (4.91)
2	37.92 (36.24)	-	-
1a	33.54 (33.54)	7.46 (7.46)	-
2a	33.35 (33.54)	12.97 (7.46)	-

The first step in the thermogravimetric curve, which occurs in the range of 35 – 105 °C, of the dinuclear complex **2×MeCN** was related to the loss of the acetonitrile molecule. On the basis of the obtained results and the ones of the elemental analysis, it was found that one molecule of acetonitrile is in the molecular structure, $[MoO_2(L^2)]_2 \times MeCN$. Further heating of the complex results in a significant weight loss in the range of 250 – 480 °C due to complex decomposition. In the case of dinuclear complex **1**, there is no coordinated or crystalline solvent present in the crystal structure and mass loss in the range 301 – 490 °C due to complex decomposition as well (Supplement, Figure D11 and D9).

TG analyses of the mononuclear complexes **1a** and **2a** showed two-step processes: desolvatation and decomposition. In the first step, weight loss of 7.46 % for **1a** and 12.97 %, for **2a** in the range of 140 – 157 °C and 107 – 150 °C, respectively, was related to the loss of coordinated methanol molecule. Desolvatation was followed by ligand decomposition and significant weight loss in the range of 325 – 445 and 260 – 450 °C (Supplement, Figure D10 and D12).

4.3. The catalytic reactions with molybdenum(VI) complexes

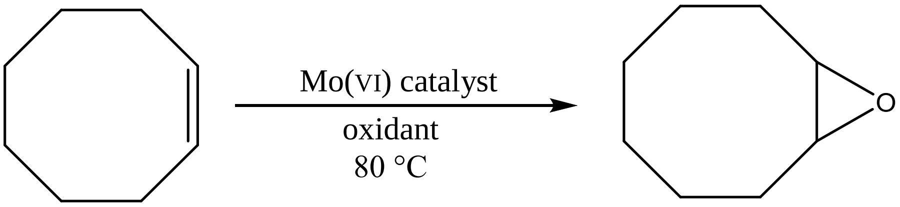
The catalytic activity of the mononuclear and dinuclear complexes was tested in the epoxidation reactions of *cis*-cyclooctene (CO) and oct-1-ene (1-O) with different oxidants (aqueous TBHP, TBHP in decane and H_2O_2). Following the rules of green chemistry, no additional organic solvent was added to reaction mixture and catalyst loading maintained low, n(Mo) : n(olefin)=0.05 mmol : 20 mmol.

As far as the solubility of the complex is concerned, at room temperature, none of the complexes (**1**, **2×MeCN**, **1a**, **2a**) was soluble by the addition of substrate. By heating the reaction mixture to a higher temperature (80 °C) and after the oxidant addition, the complexes were dissolved. Depending on the oxidant used, there was a difference in the solubility of the individual complex. All the complexes showed relatively good solubility in aqueous TBHP, but lower solubility when H_2O_2 was added to the reaction mixture, while almost complete complex solubility was noticed when TBHP in decane was used. By using aqueous TBHP and H_2O_2, two phases were observed in reaction mixture, aqueous and organic one.

The conversion of substrates and the formation of the product were calculated from the calibration curves relative to acetophenone (Supplement, Figure D14-17).

4.3.1. Epoxidation of cis-cyclooctene

The main product of catalysed reaction of *cis*-cyclooctene was cyclooctene oxide, which was present in the organic phase of the reaction mixture (Scheme 4).



Scheme 4. Cyclooctene epoxidation catalysed by molybdenum complexes.

The results of catalysis for each oxidant used are summarised in Table 4.

Table 4. Results of the cyclooctene epoxidation catalysed with Mo(VI) complexes in the presence of three different oxidants.

Mo(VI) catalyst	oxidant	Conv.[c] CO / %	Selectivity[d] (epoxide) / %	$TOF_{20\ min}$[e] / h^{-1}	TON[f]
1[a]	aqueous TBHP	94	83	370	378
1a[a]		93	90	406	365
2 × MeCN[a]		90	82	346	357
2a[a]		91	87	332	362
1[b]	TBHP in decane	99	91	1005	419
1a[b]		99	92	9415	400
2 × MeCN[b]		99	93	9556	400
2a[b]		99	89	2398	400
1[a]	H_2O_2	12.4	20.3	13	49
2 × MeCN[a]		10.4	26	7	41
2a[a]		6.7	49	16	27

[a] Reaction conditions: time, 5 h; temperature, 80 °C, [Mo]/cyclooctene/oxidant molar ratio: 0.25/100/200. [b] Reaction conditions: time, 30 min; temperature, 80 °C, [Mo]/cyclooctene/oxidant molar ratio: 0.25/100/200. [c] CO consumed at the end of reaction. [d] Formed epoxide per converted olefin at the end of reaction. [e] *n*(cyclooctene) transformed/*n*(catalyst)/time(h) at 20 minutes. [f] *n*(cyclooctene) transformed/*n*(catalyst) at the end of reaction.

In reactions with aqueous TBHP as oxidant, dinuclear and mononuclear complexes showed high conversion values, 91–94 %, while selectivity ranges from 82 to 90 %. Water from aqueous TBHP does not act as a solvent since the molybdenum(VI) complexes are soluble in the substrate and not in water. Complexes **1** and **1a** were more soluble in the reaction media and showed the highest activity, therefore initial TOF value is higher for complex **1a** (406 h^{-1}) while the lowest one is for complex **2a** (332 h^{-1}). Comparing the kinetic profile of mononuclear and dinuclear complexes (Figure 12) it was observed that the mononuclear complex **1a** has the highest activity only in the first 20 min of reaction, after 20 min the corresponding dinuclear complex **1** has the highest activity. As for the complexes **2 × MeCN** and **2a**, they have lower activity then complexes **1** and **1a**, and mononuclear **2a** is showing higher activity than the corresponding dinuclear complex.

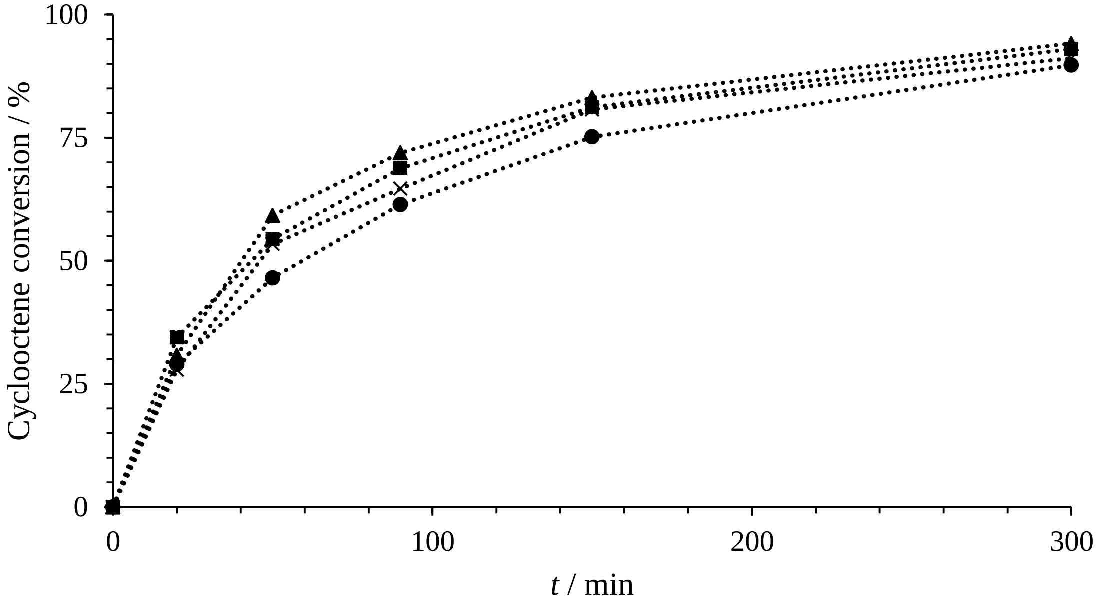


Figure 12. Converted cyclooctene *vs*. time with molybdenum(VI) complexes as catalysts and aqueous TBHP as oxidant: ▲ complex **1**, ■ complex **1a**, ● complex **2×MeCN**, × complex **2a**. Reaction conditions: catalyst/cyclooctene/aqueous TBHP molar ratio: 0.25/100/200, *T* = 353 K.

TBHP in decane as oxidant showed quicker results than TBHP in water. Water seems to inhibit partially the reactivity of the catalysts or does not help all the reactants to be efficient (several H-bonds are possible with water and not with decane). Since the epoxidation reaction is finished within 30 min when TBHP in decane is used as an oxidant, samples were taken at different timing than for the reactions with H_2O_2 and aqueous TBHP. However, all four complexes show very high activity (99 % of cyclooctene conversion) and selectivity towards epoxide (around 92 %). Initial TOF values are very high considering low catalyst loading (0.25 %). The highest TOF value is for complex **2×MeCN** (9556 h^{-1}) and the lowest (1005 h^{-1}) for complex **1**.

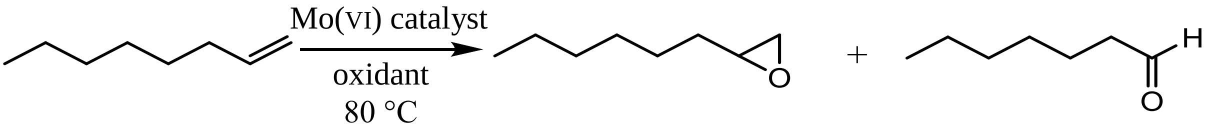
In further reactions, complex **1a** was not used as a catalyst because of the low yield in the synthesis. The synthesis itself did not follow all the principles of green chemistry due to the use of an increased amount of solvent and a long time of product formation.

With H_2O_2 as oxidant, the catalytic efficiency is not high as with TBHP (in water or in decane). Complex **1** has the highest conversion of 12.4 %, while mononuclear complex **2a** has the lowest value of 6.7 %. In kinetic profile (Supplement, Figure D19) it was again observed that mononuclear complex **2a** showed the highest activity in first 20 min of reaction, TOF value is the highest for complex **2a** (16 h^{-1}) and the lowest for complex **2×MeCN** (7 h^{-1}). As the reaction time increases the activity of the complex **2a** decreases but the activity of dinuclear complexes **1** and **2×MeCN** increases.

The more soluble complexes in reaction mixture showed higher activity. In general, dinuclear complexes **1** and **2×MeCN** showed higher conversion of *cis-cyclooctene*, but mononuclear complexes **1a** and **2a** showed higher selectivity towards cyclooctene oxide. This suggests that the faster formation of the catalytically active pentacoordinated [MoO_2L] species is promoted when the (pre)catalysts are more soluble and when the reaction media does not give the possibility of hydrogen bonds with the reactants.[4]

4.3.2. *Epoxidation of oct-1-ene*

The main product of catalysed epoxidation of oct-1-ene is 1,2-epoxyoctane, which is present in the organic phase of the reaction mixture, and heptan-1-al (due to oxidative C=C cleavage) in small but relevant quantity (Scheme 5).



Scheme 5. Oct-1-ene epoxidation catalysed by molybdenum complexes.

In reactions where the oct-1-ene is a substrate, there is a greater difference in the activity of the molybdenum complexes as a catalyst than with cyclooctene. The reason for the larger difference in catalyst activity is the lower reactivity of oct-1-ene in epoxidation reactions, as reported in the literature.[21]

Catalytic results and important parameters for each oxidant used are summarised in Table 5, and results of the oct-1-ene epoxidation catalysed with Mo(VI) complexes with selectivity towards heptan-1-al are presented in Supplement, Figure D26.

Table 5. Results of the oct-1-ene epoxidation catalysed with Mo(VI) complexes in the presence of three different oxidants.

Mo(VI) catalyst	oxidant	Conv.[c] 1-O / %	Selectivity[d] (epoxide) / %	TOF$_{20\ \mathrm{min}}$[e]/ h^{-1}	TON[f]
1[a]	aqueous TBHP	12	41	51	49
2×MeCN[a]		6	20	30	24
2a[a]		17	3	95	69
1[b]	TBHP in decane	19	63	146	280
2×MeCN[b]		76	66	889	304
2a[b]		77	56	5760	301
1[a]	H_2O_2	11	0.37	48	44
2×MeCN[a]		10	0.71	40	41
2a[a]		8	0.36	16	33

[a] Reaction conditions: time, 5 h; temperature, 80 °C, [Mo]/oct-1-ene/oxidant molar ratio: 0.25/100/200. [b] Reaction conditions: time, 30 min; temperature, 80 °C, [Mo]/oct-1-ene/oxidant molar ratio: 0.25/100/200. [c] 1-O consumed at the end of reaction. [d] Formed epoxide per converted olefin at the end of reaction. [e] *n*(oct-1-ene) transformed/*n*(catalyst)/time(h) at 20 minutes. [f] *n*(oct-1-ene transformed)/*n*(catalyst) at the end of reaction.

In reactions where aqueous TBHP was used as the oxidant, conversion values vary from 6 to 17 %, as for selectivity towards 1,2-epoxyoctane, ranges from 3 to 41 %. In comparison with *cis*-cyclooctene as substrate (conversion over 90 % and selectivity over 80 %), obtained values of conversion and selectivity are dramatically low. Results confirm that oct-1-ene has low reactivity towards epoxidation, in aqueous media, and greater difference among catalysts can be observed. Mononuclear complex **2a** was more soluble in reaction mixture than dinuclear complexes **1** and **2×MeCN**, and it showed the highest activity. TOF value for complex **2a** is 95 h^{-1}, and for complexes **1** and **2×MeCN** are 51 h^{-1} and 30 h^{-1}.

As stated before, reactions with TBHP in decane are finished within 30 min, but with oct-1-ene as substrate and complex **1** as catalyst reaction was slower and it was monitored for 5 h, with all oxidants. After 5 h of reaction, 76 % of the oct-1-ene reacted and 10 % of the product formed was 1,2-epoxyoctane. Compared to complexes **2×MeCN** and **2a** which show the same percentage of conversion after 30 min of reaction, the activity of complex **1** is not high. As for complexes **2×MeCN** and **2a**, mononuclear complex showed again higher activity (Supplement, Figure D21), with TOF value of 5760 h^{-1}, but lower selectivity towards epoxide (56 %).

The lowest values of selectivity towards 1,2-epoxyoctane were obtained in reactions with H_2O_2 as oxidant. None of the catalysts has a selectivity over 1 %. In terms of conversion and TOF value, complex **1** obtained the highest values (11 %, 48 h^{-1}). Reason for complex **1** to obtain highest value of conversion in case of 2-aminobenzoylhydrazone derived complexes, dinuclear complexes transform more easily to the pentacoordinated species.[14]

In all epoxidation reactions where oct-1-ene was a substrate, the catalyst with highest TOF value was also the one with the highest conversion values, but in reactions with cyclooctene, the catalyst which had the highest TOF value had the highest values of selectivity.

§ 5. CONCLUSION

Four dioxomolybdenum(VI) complexes using two different *ONO* tridentate hydrazone ligands were synthesized and characterized. In acetonitrile, dimer complexes $[MoO_2(L^1)]_2$ and $[MoO_2(L^2)]_2 \times MeCN$ were obtained, and in methanol solution, mononuclear complexes, $[MoO_2(L^1)(MeOH)]$ and $[MoO_2(L^2)(MeOH)]$ were prepared. All four complexes obtain octahedral geometry where hydrazone ligand is coordinated in deprotonated L^{2-} form through the phenolic-oxygen (deprotonated 2-hydroxyl oxygen), imine-nitrogen and the oxygen atom from hydrazone part of the ligand. Sixth coordination site is occupied by an oxygen atom from methanol molecule in case of mononuclear complex or by nitrogen atom of the bridging aminobenzoylhydrazone of the neighbouring complex.

The synthesized complexes can act as (pre)catalysts in epoxidation of olefins under organic solvent-free conditions. Cyclooctene is better model substrate for epoxidation reactions than oct-1-ene, since it is more reactive and the only product of reaction was cyclooctene oxide. Three different oxidizing agents were used in catalytic reactions: aqueous TBHP, TBHP in decane and hydrogen peroxide. The highest values of conversion (99 %) were obtained in reactions where TBHP in decane was used as oxidant due to great solubility of complexes. In reactions with aqueous TBHP, a slight difference in conversion among complexes was observed. Dimeric complexes showed higher conversion values than monomeric ones. This can be attributed to the easier formation of the mononuclear pentacoordinated $[MoO_2L]$ species due to weak donor properties of the coordinated amino group. Based on the obtained catalytic results, it can be observed that the position of the amino group on the phenyl ring influences the catalytic properties of the complex and 2-aminobenzoylhydrazone derived complexes transform more easily to pentacoordinated species.

§ 6. LIST OF ABBREVIATIONS AND SYMBOLS

1-O – oct-1-ene

3OMe – 3-methoxysalicylaldehyde 4-hydroxybenzhydrazone

4OMe – 4-methoxysalicylaldehyde 4-hydroxybenzhydrazone

acac – acetylacetonate

cat – catalyst

CO – *cis*-cyclooctene

CON_R – conversion

D – donor molecule

EA – elemental analysis

EtOH - ethanol

GC – gas chromatography

ATR – Attenuated Total Reflectance

L – ligand

MeCN – acetonitrile

MeOH – methanol

P – product

R – reactant

Q – by-product

S – selectivity

TG – thermogravimetric

TOF – turn-over frequency

TON – turn-over number

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§ 8. APPENDIX

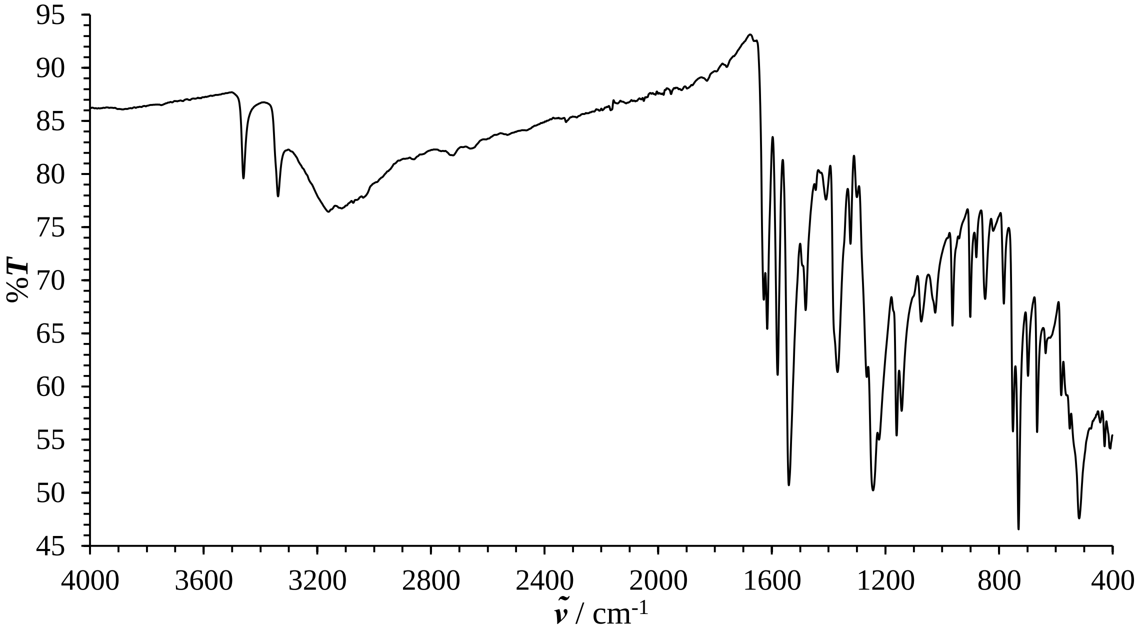

Figure D1. IR spectra of the ligand H_2L^1.

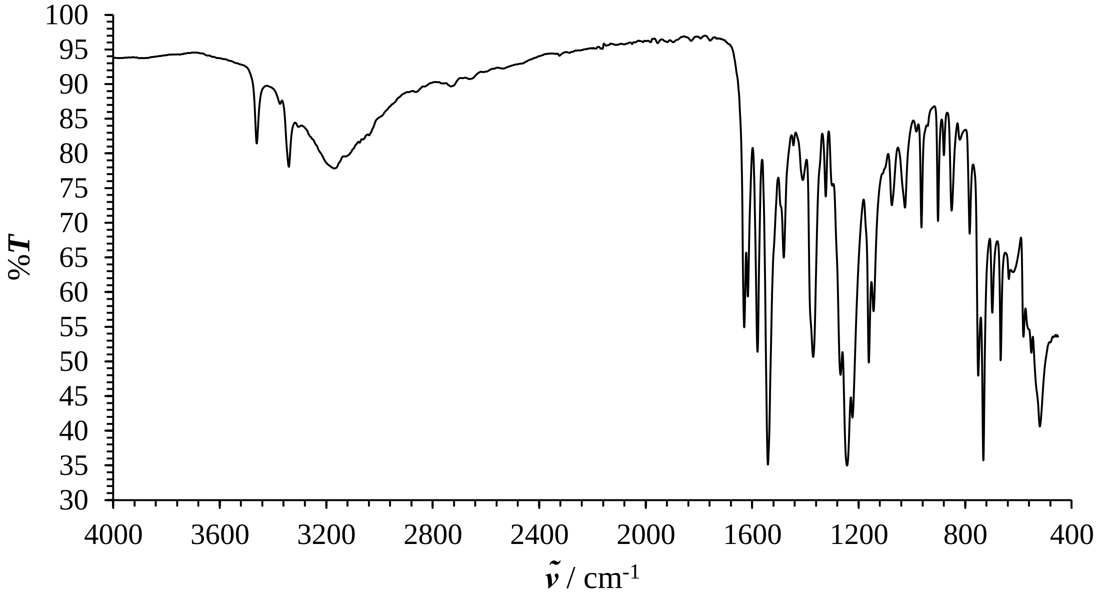

Figure D2. IR spectra of mechanochemically synthesised H_2L^1.

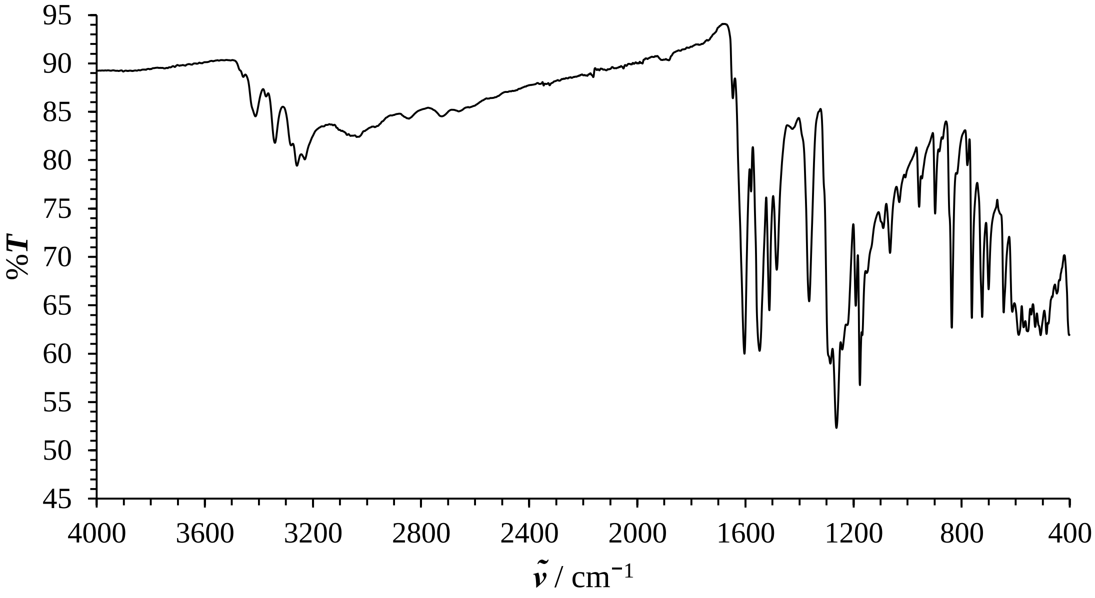

Figure D3. IR spectra of the ligand H_2L^2.

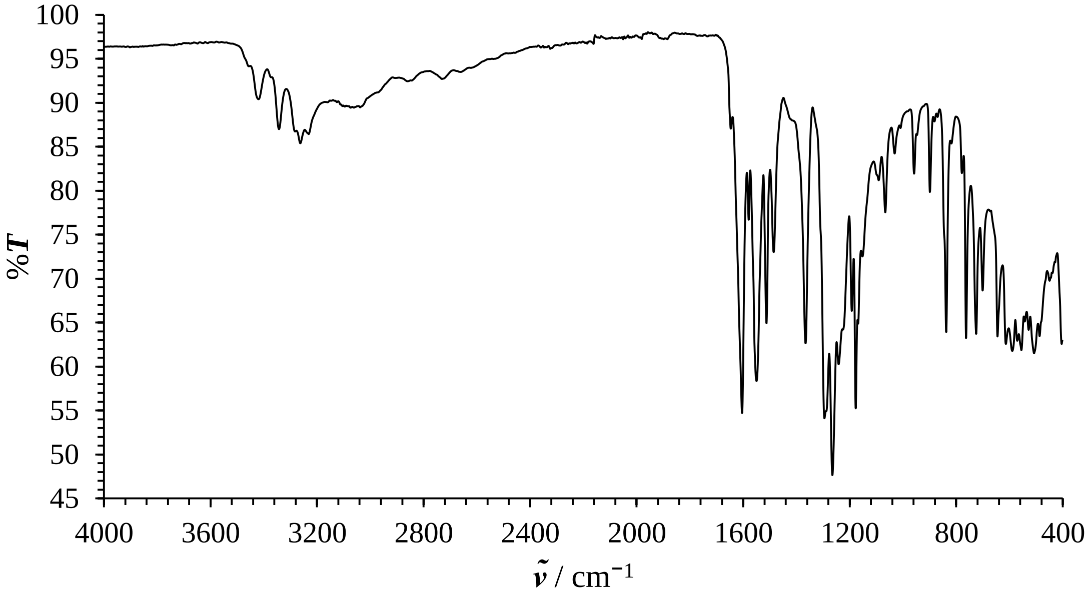

Figure D4. IR spectra of mechanochemically synthesised H_2L^2.

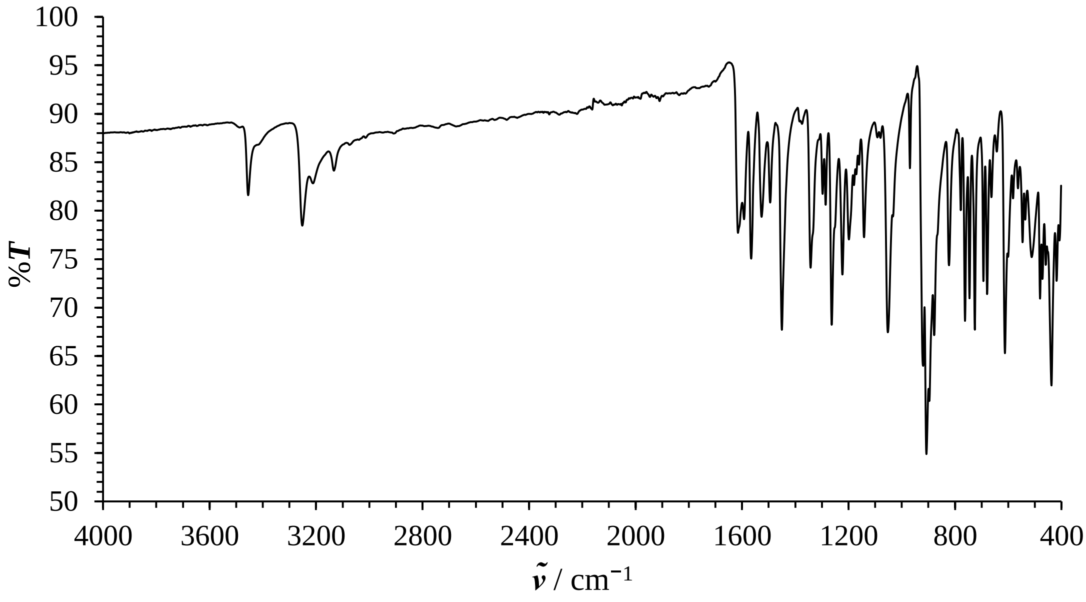

Figure D5. IR spectra of the complex **1**.

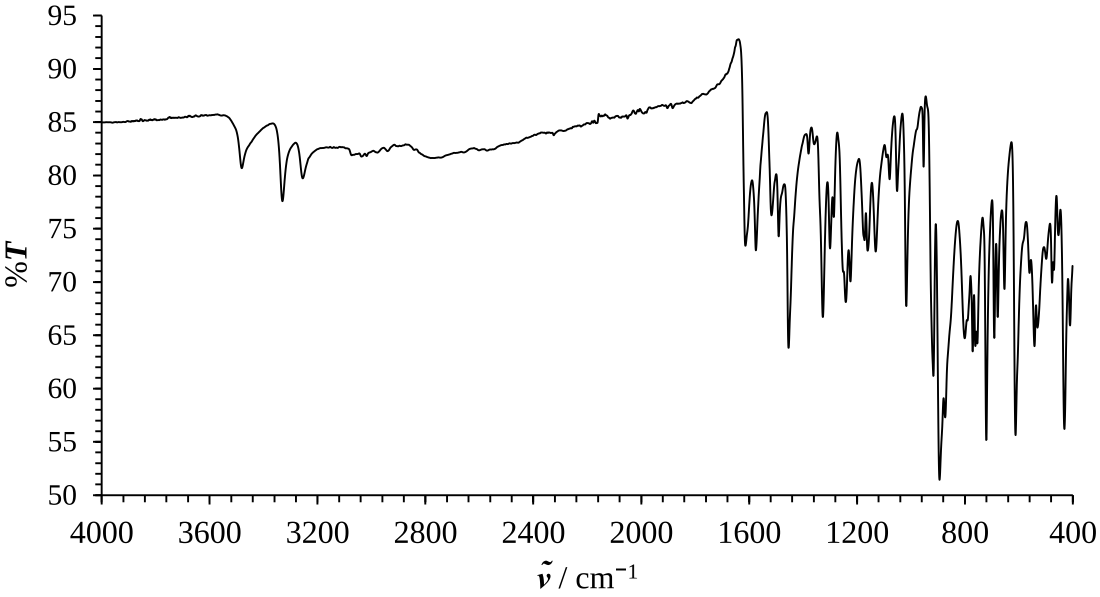

Figure D6. IR spectra of the complex **1a**.

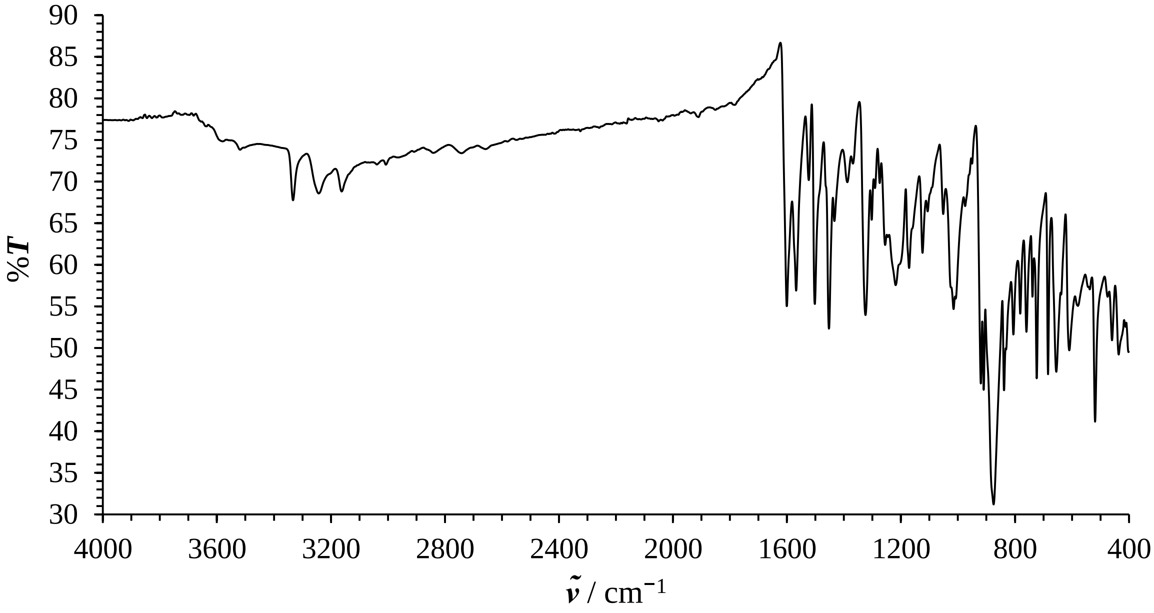

Figure D7. IR spectra of the complex **2×MeCN**.

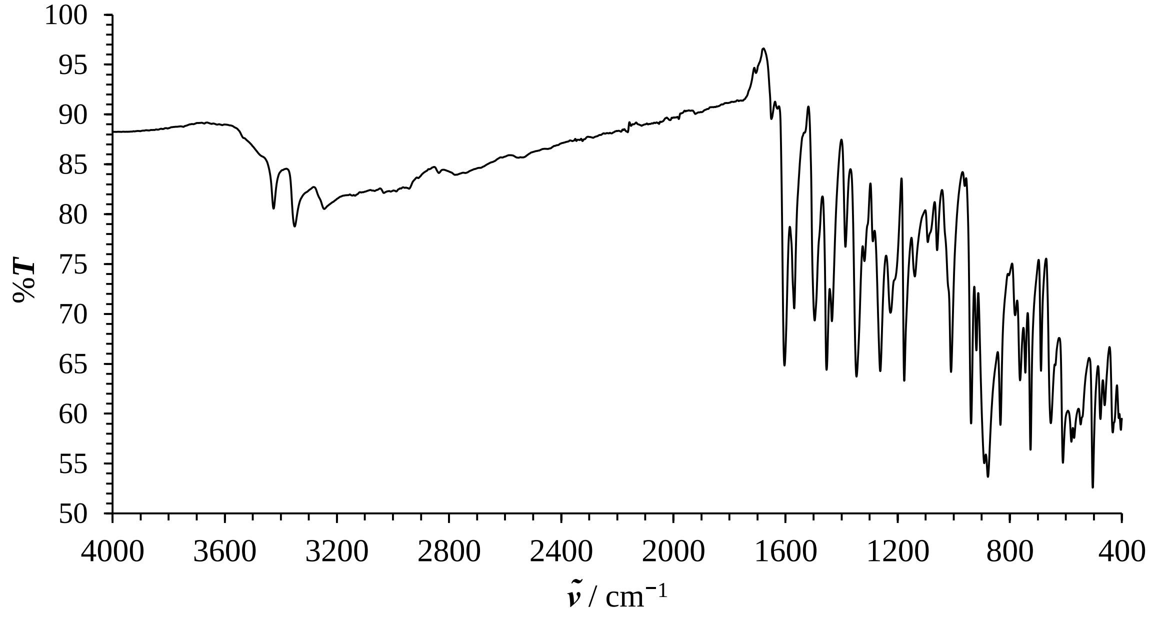

Figure D8. IR spectra of the complex **2a**.

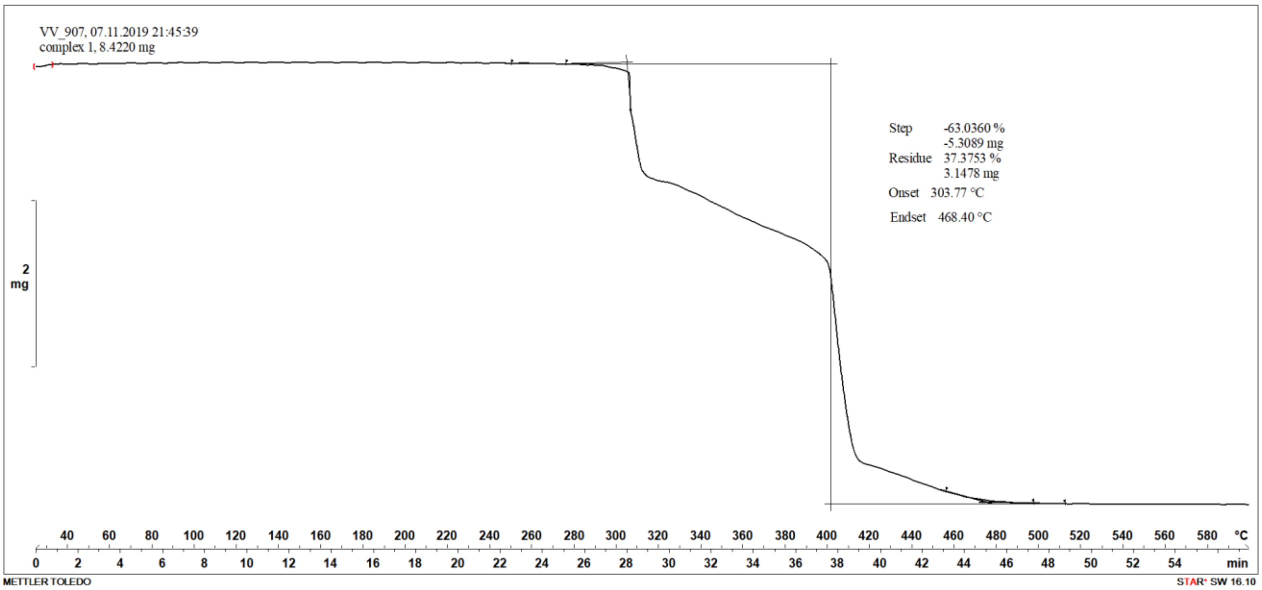

Figure D9. Thermogram of the complex **1**.

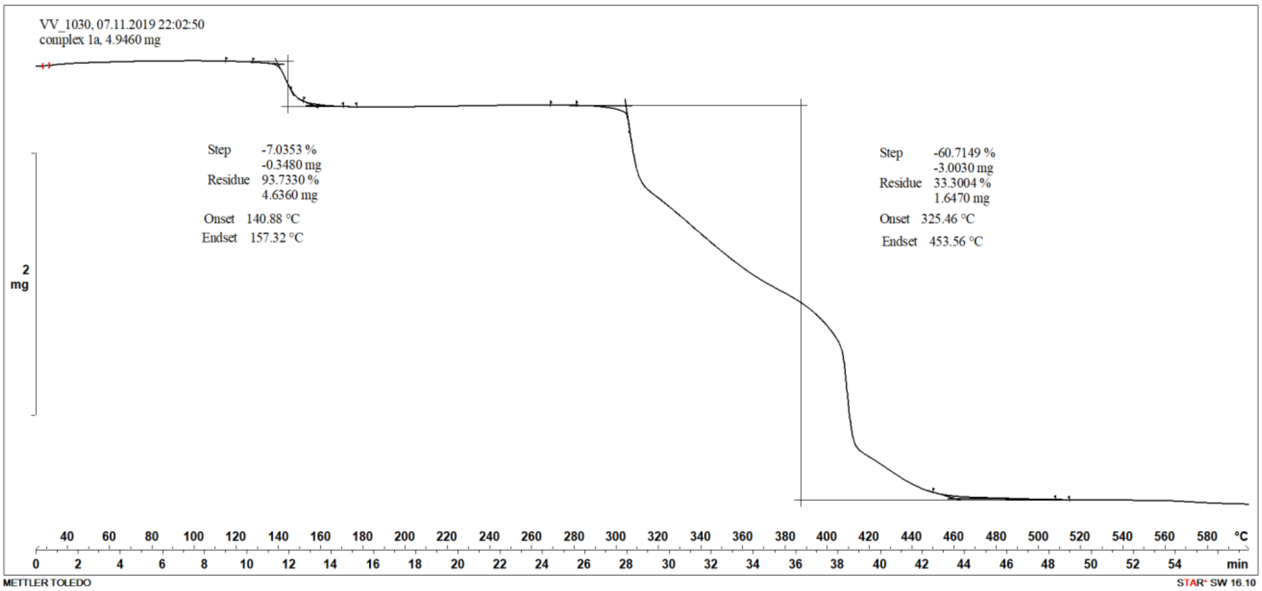

Figure D10. Thermogram of the complex **1a**.

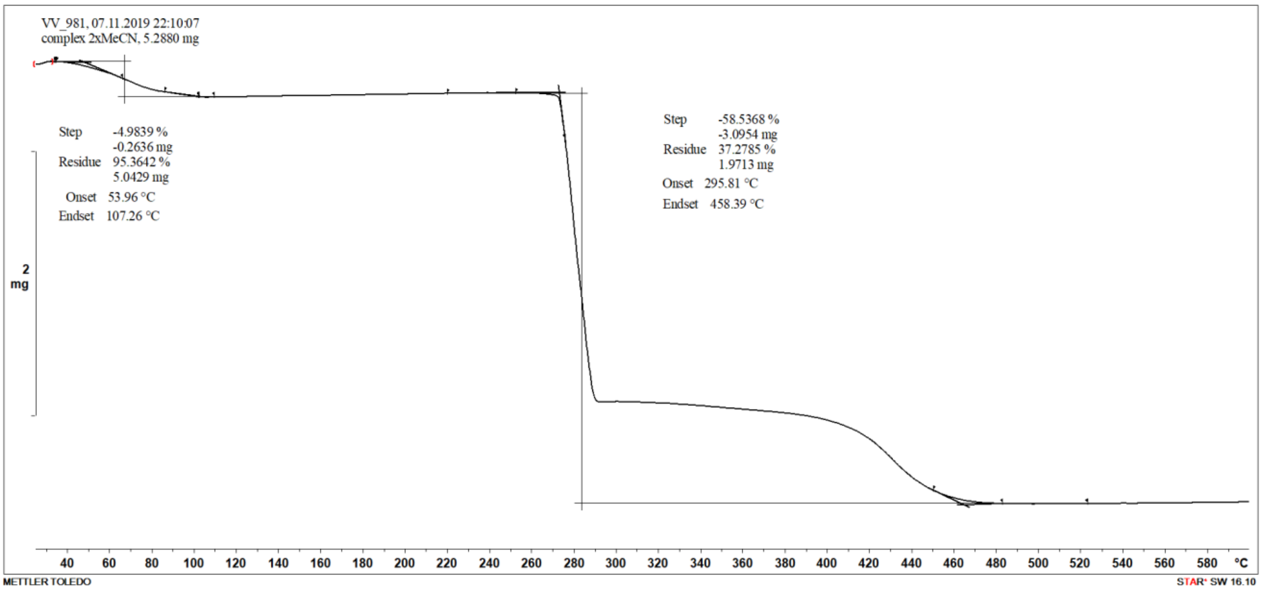

Figure D11. Thermogram of the complex **2×MeCN**.

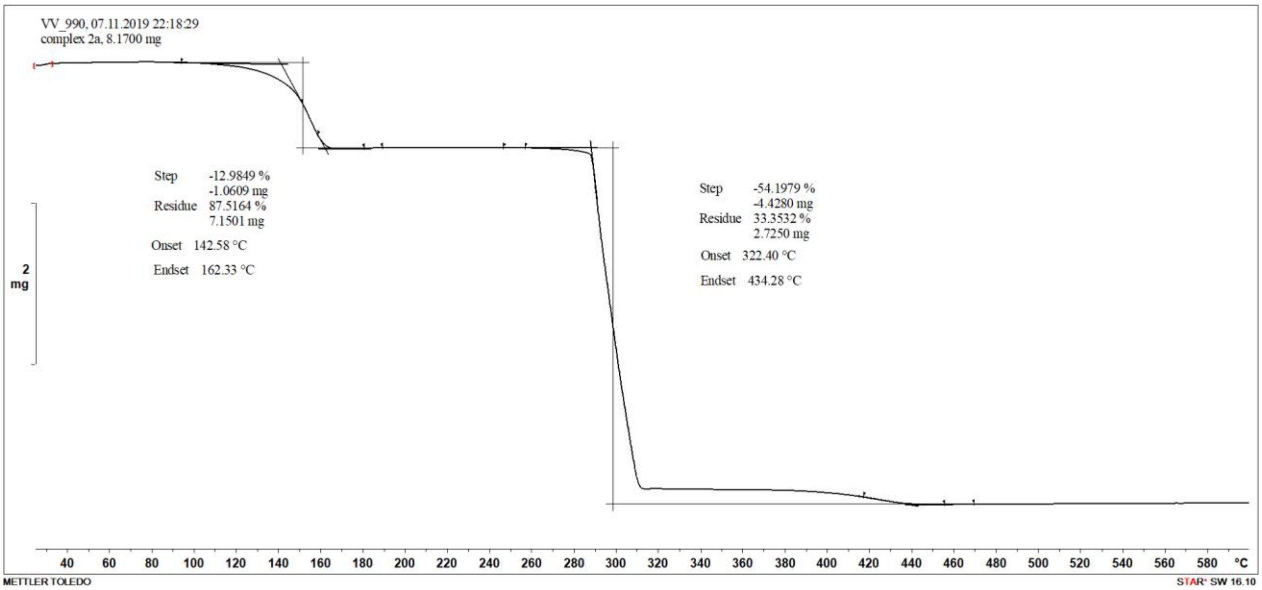

Figure D12. Thermogram of the complex **2a**.

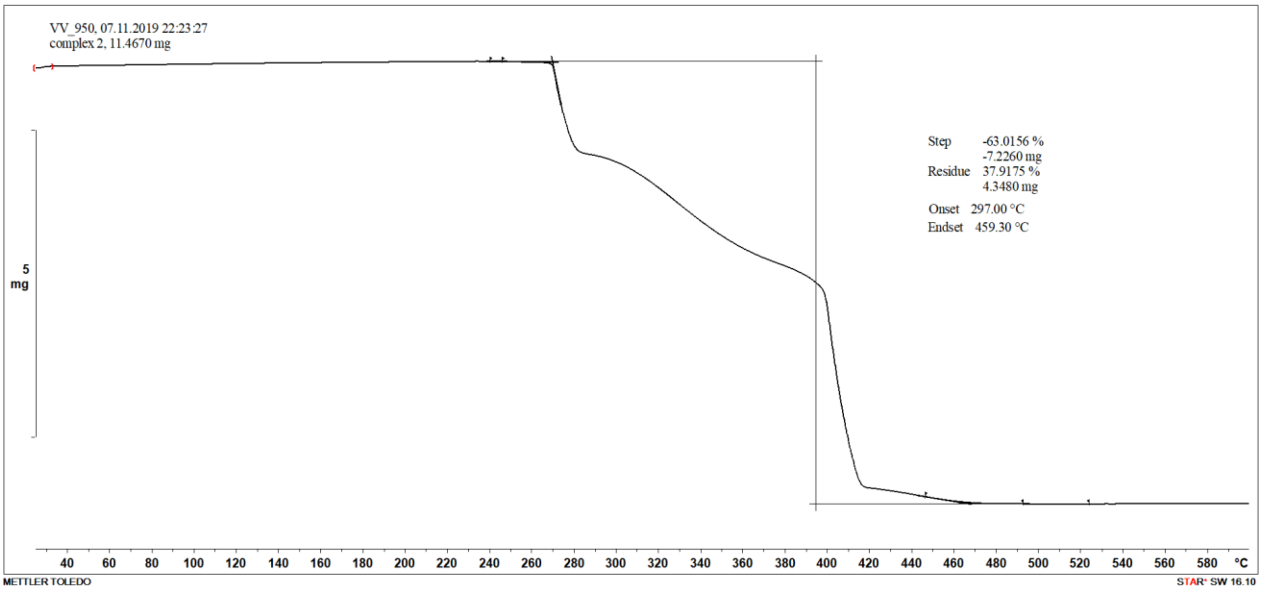

Figure D13. Thermogram of the complex **2**.

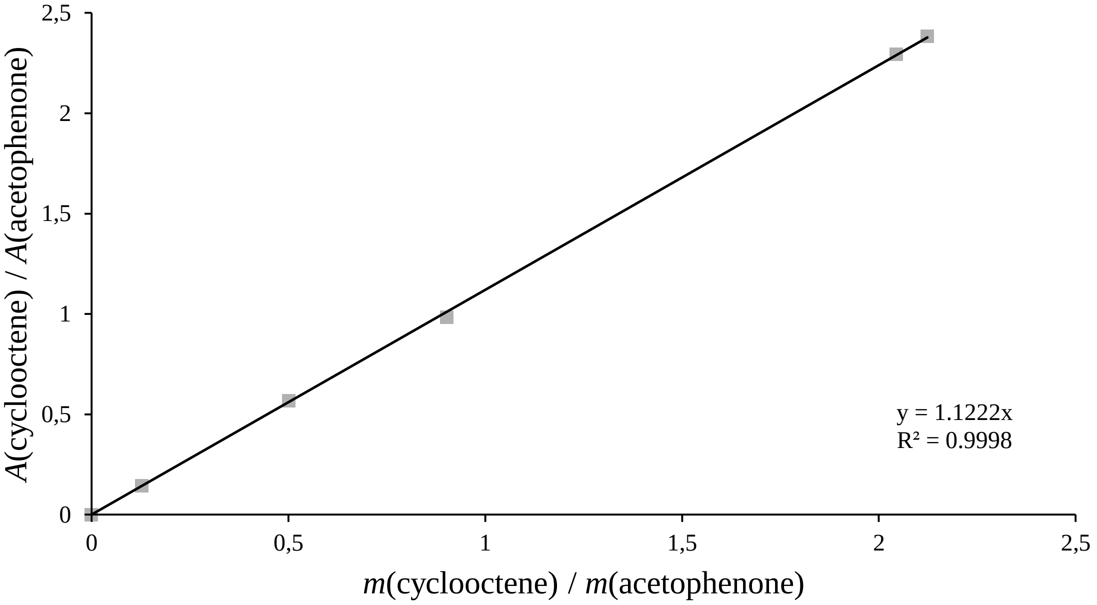

Figure D14. Calibration curve of cyclooctene obtained by GC measurement with acetophenone as an internal standard.

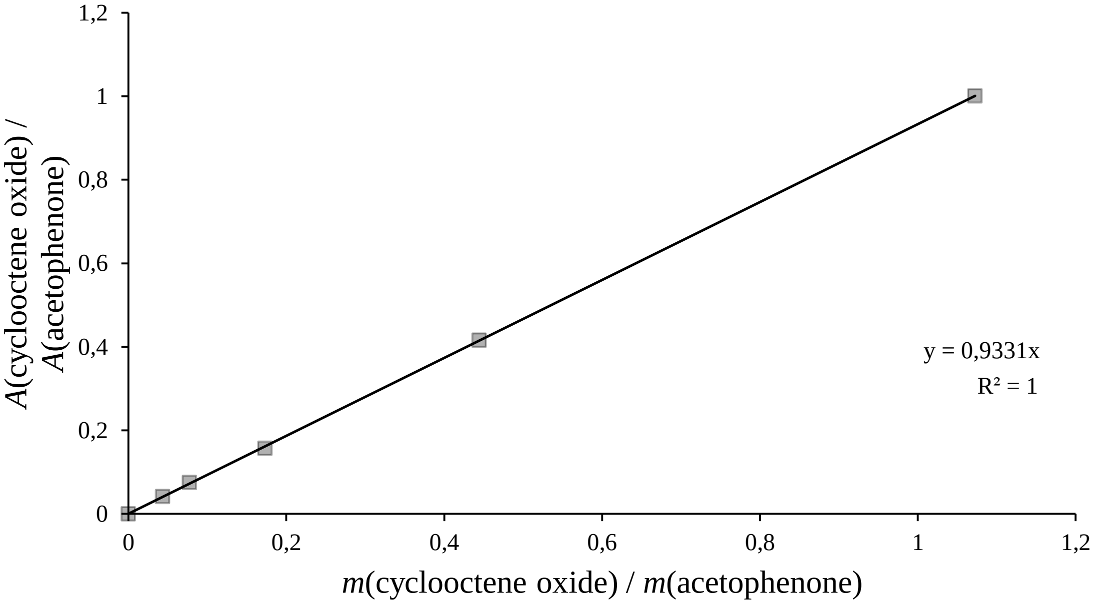

Figure D15. Calibration curve of cyclooctene oxide obtained by GC measurement with acetophenone as an internal standard.

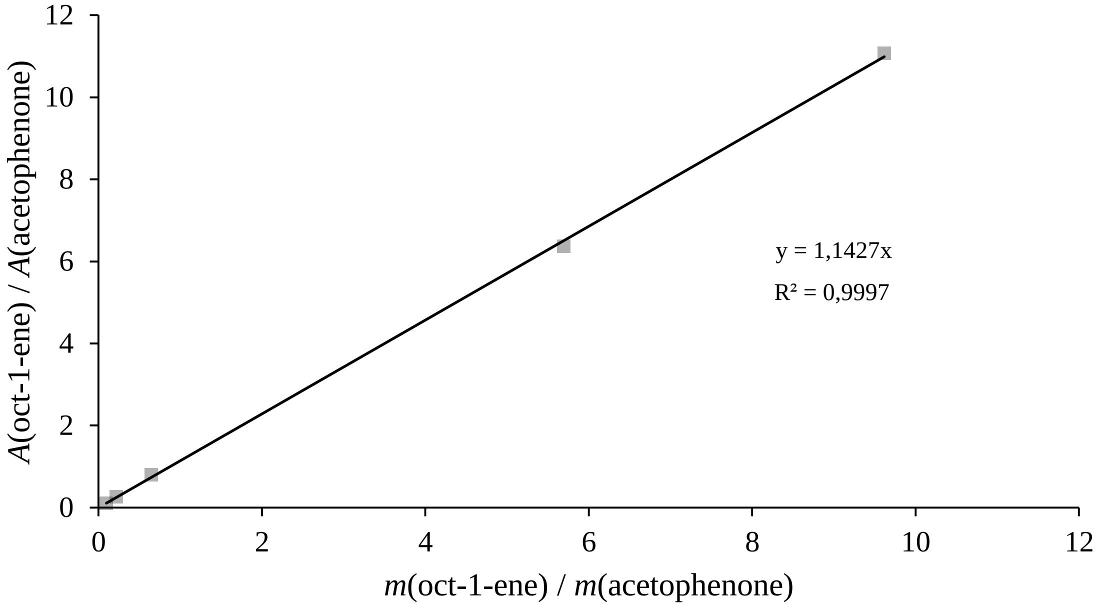

Figure D16. Calibration curve of oct-1-ene obtained by GC measurement with acetophenone as an internal standard.

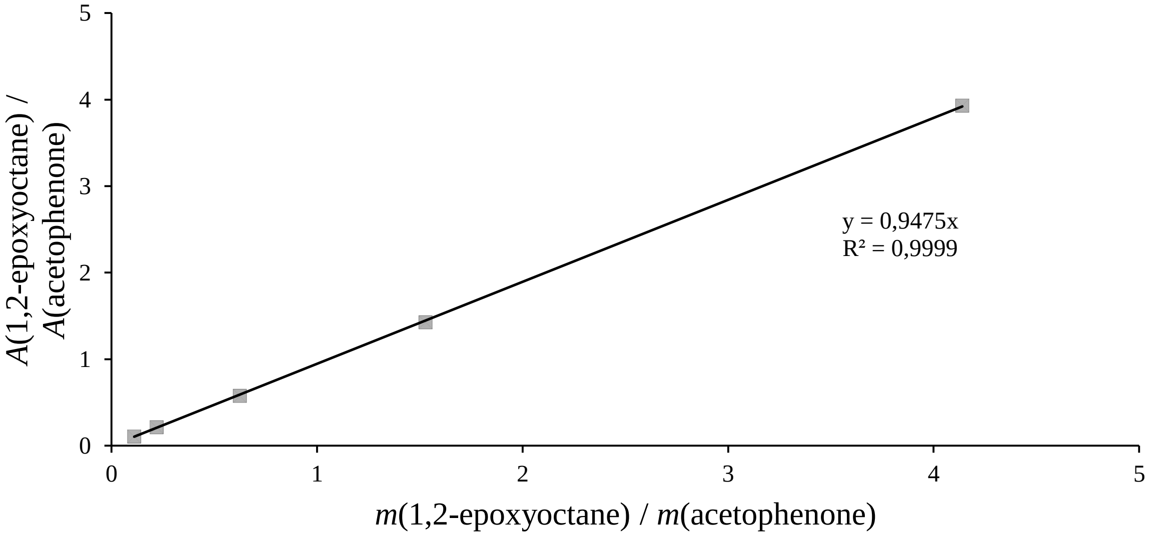

Figure D17. Calibration curve of 1,2-epoxyoctane obtained by GC measurement with acetophenone as an internal standard.

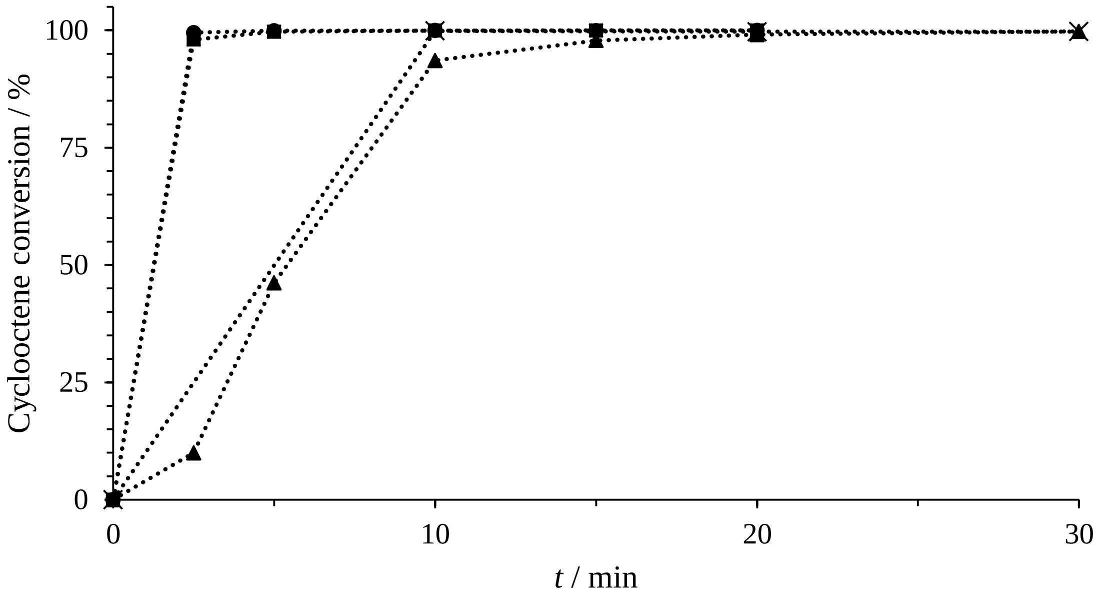

Figure D18. Converted cyclooctene *vs*. time with molybdenum(VI) complexes as catalysts and TBHP in decane as oxidant: ▲ complex **1**, ■ complex **1a**, ● complex **2×MeCN**, × complex **2a**. Reaction conditions: catalyst/cyclooctene/TBHP molar ratio: 0.25/100/200, *T* = 353 K.

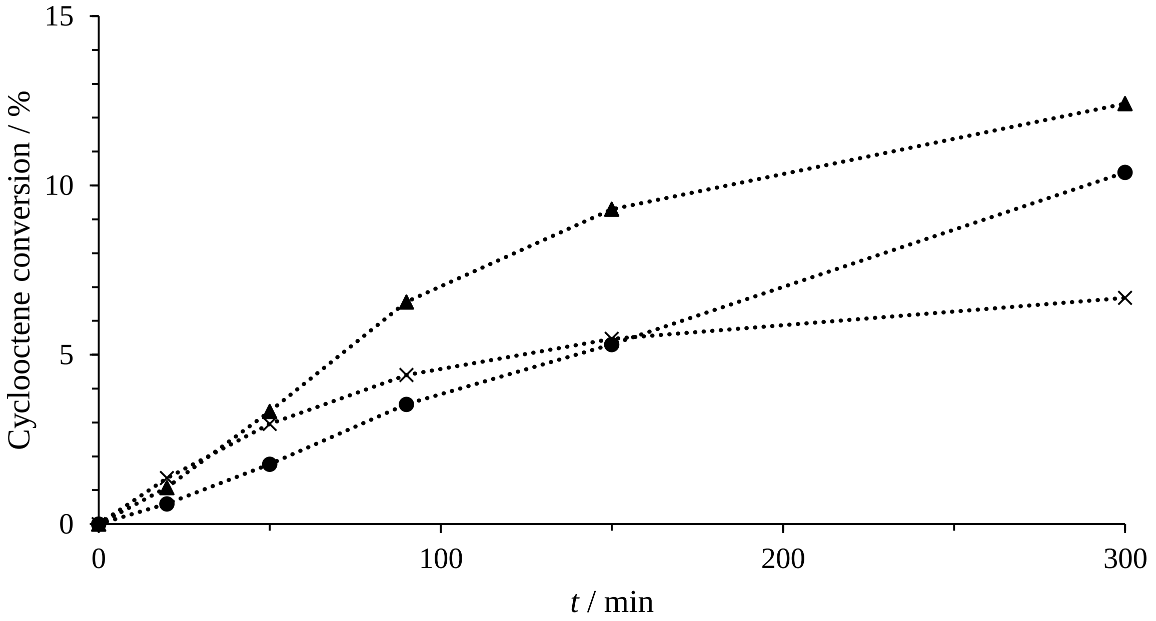

Figure D19. Converted cyclooctene *vs*. time with molybdenum(VI) complexes as catalysts and H_2O_2 as oxidant: ▲ complex **1**, ● complex **2×MeCN**, × complex **2a**. Reaction conditions: catalyst/cyclooctene/H_2O_2 molar ratio: 0.25/100/200, *T* = 353 K.

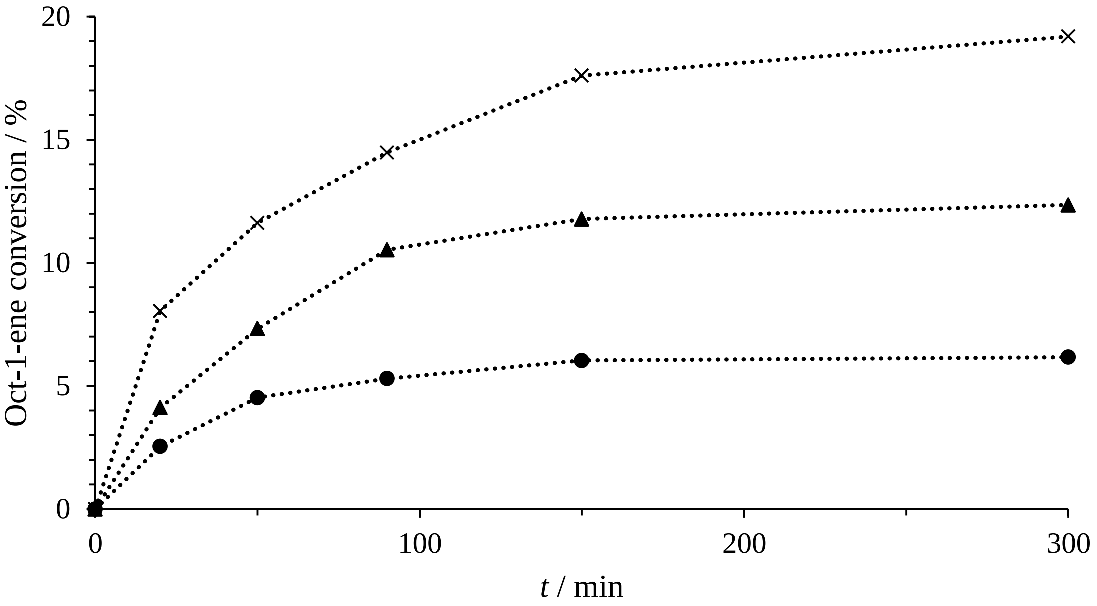

Figure D20. Converted oct-1-ene *vs*. time with molybdenum(VI) complexes as catalysts and aqueous TBHP as oxidant: ▲ complex **1**, ● complex **2×MeCN**, × complex **2a**. Reaction conditions: catalyst/oct-1-ene/TBHP molar ratio: 0.25/100/200, *T* = 353 K.

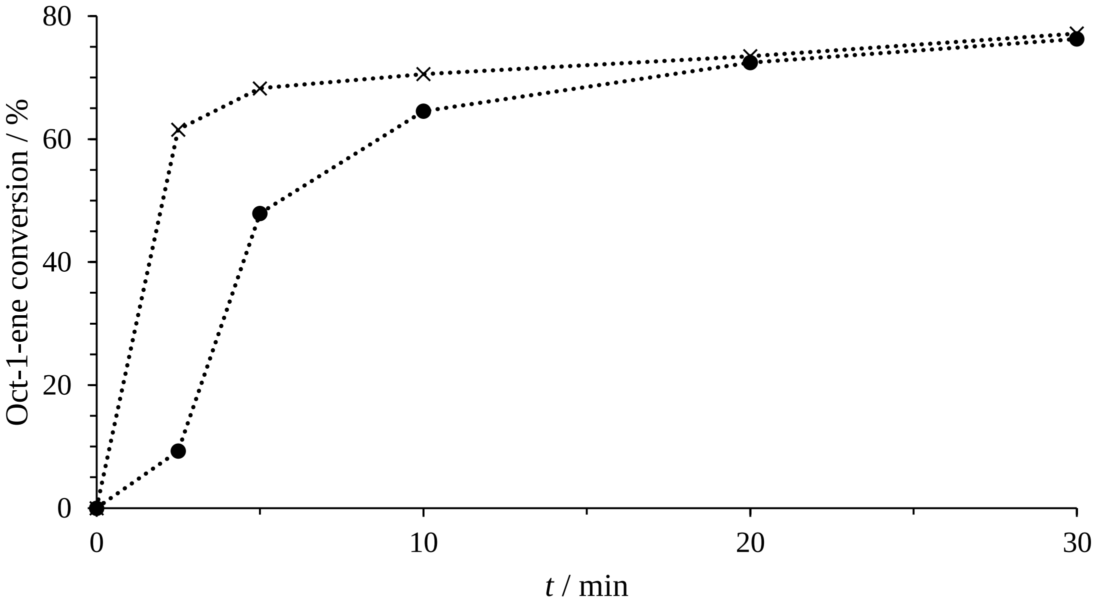

Figure D21. Converted oct-1-ene *vs*. time with molybdenum(VI) complexes as catalysts and TBHP in decane as oxidant: ● complex **2×MeCN**, × complex **2a**. Reaction conditions: catalyst/oct-1-ene/TBHP molar ratio: 0.25/100/200, *T* = 353 K.

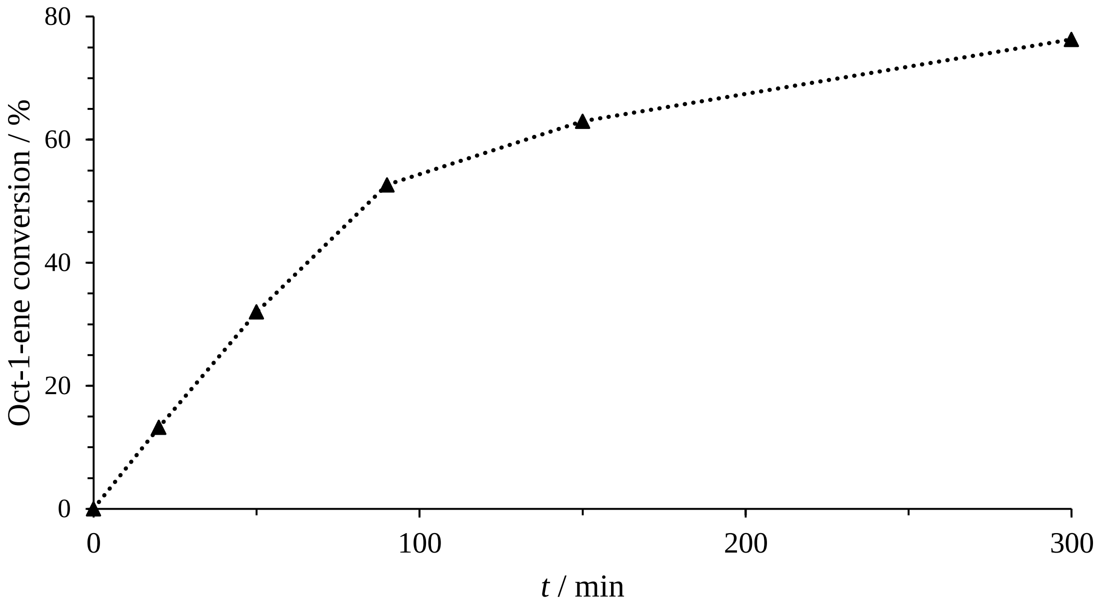

Figure D22. Converted oct-1-ene *vs*. time with molybdenum(VI) complex as catalyst and TBHP in decane as oxidant: ▲ complex **1**. Reaction conditions: catalyst/oct-1-ene/TBHP molar ratio: 0.25/100/200, T = 353 K.

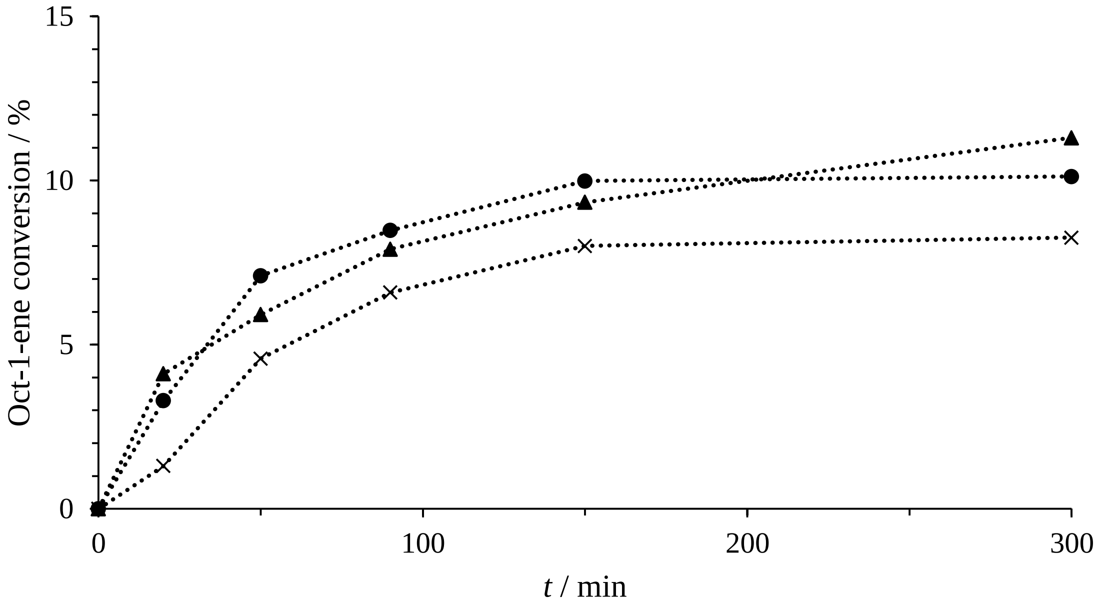

Figure D23. Converted oct-1-ene *vs*. time with molybdenum(VI) complexes as catalysts and H_2O_2 as oxidant: ▲ complex **1**, ● complex **2×MeCN**, × complex **2a**. Reaction conditions: catalyst/oct-1-ene/H_2O_2 molar ratio: 0.25/100/200, T = 353 K.

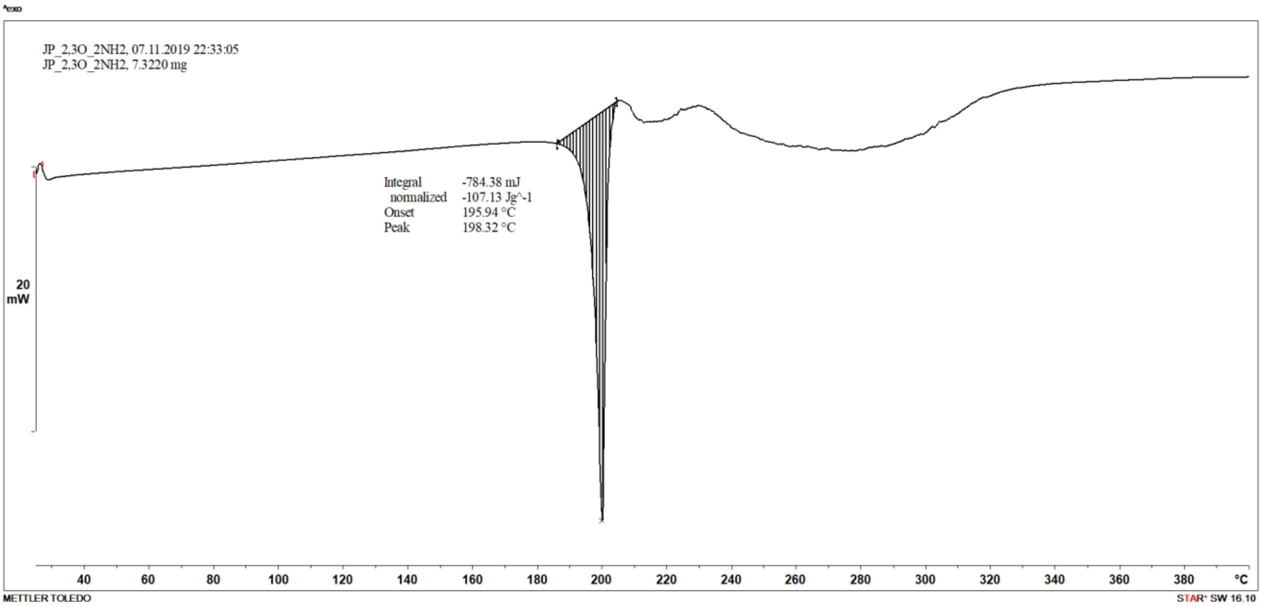

Figure D24. Differential scanning calorimetry thermogram of the ligand H_2L^1.

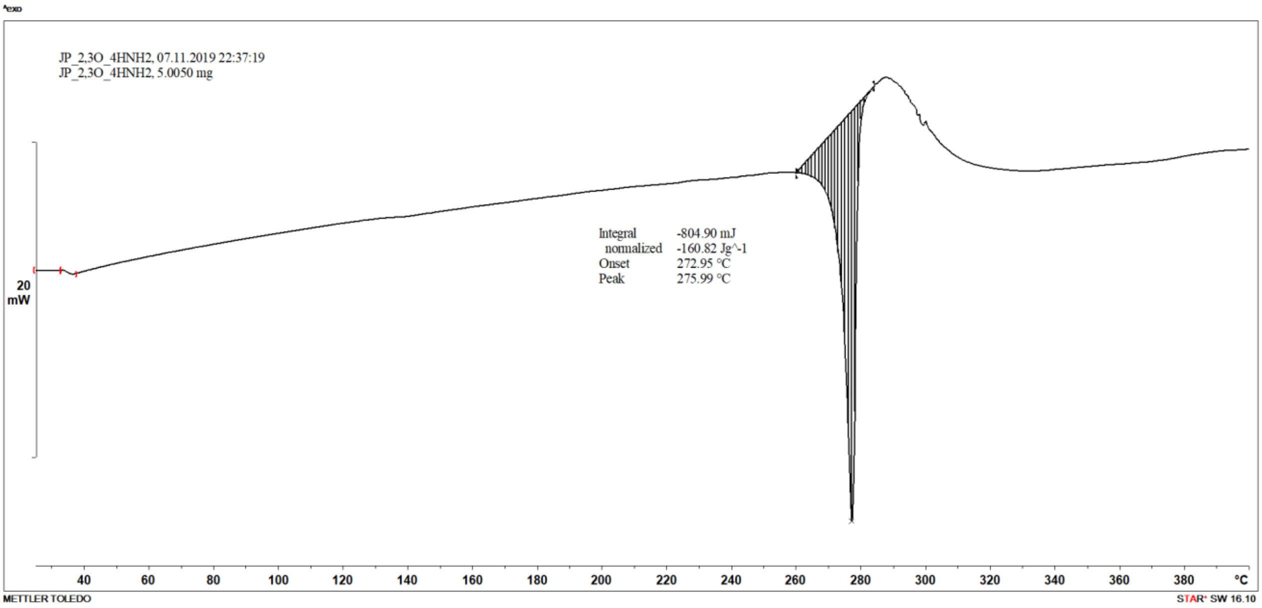

Figure D25. Differential scanning calorimetry thermogram of the ligand H_2L^2.

Mo(VI) catalyst	oxidant	Conv.[c] 1-O / %	Selectivity[d] (heptan-1-al) / %	TOF$_{20\ \mathrm{min}}$[e]/ h^{-1}	TON[f]
1[a]	aqueous TBHP	12	2.8	51	49
2×MeCN[a]		6	6.3	30	24
2a[a]		17	2	95	69
1[b]	TBHP in decane	19	17	146	280
2×MeCN[b]		76	0.7	889	304
2a[b]		77	22	5760	301
1[a]	H_2O_2	11	0.2	48	44
2×MeCN[a]		10	0.35	40	41
2a[a]		8	0	16	33

Figure D26. Results of the oct-1-ene epoxidation catalysed with Mo(VI) complexes in the presence of three different oxidants with selectivity towards heptan-1-al.

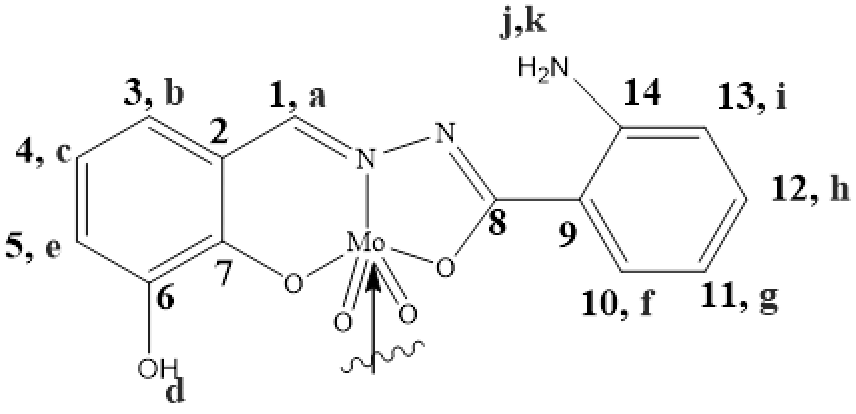

Figure D27. Structure of complex **1** with NMR labels.

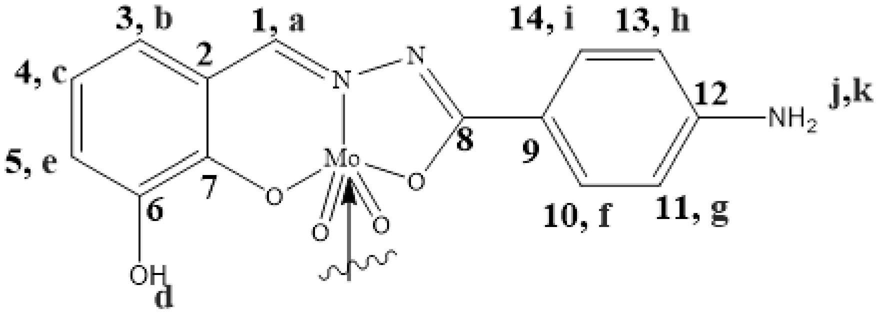

Figure D28. Structure of complex **2×MeCN** with NMR labels.

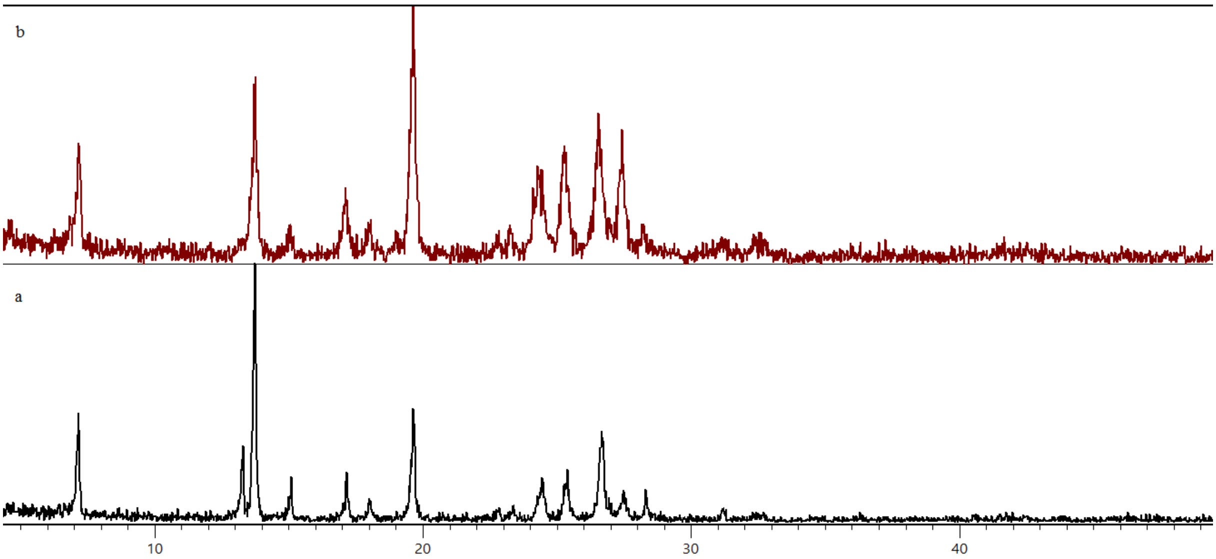

Figure D29. Compared diffractograms of **H_2L^1**, (a) solution based synthesis; (b) mechanochemical synthesis.

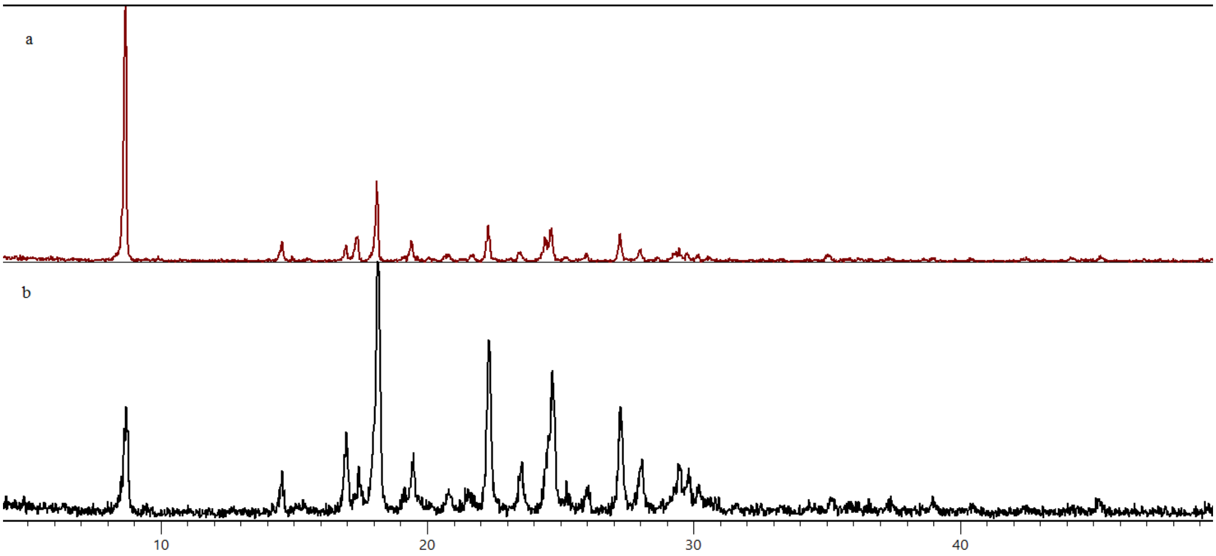

Figure D30. Compared diffractograms of **H_2L^2**, (a) solution based synthesis; (b) mechanochemical synthesis.

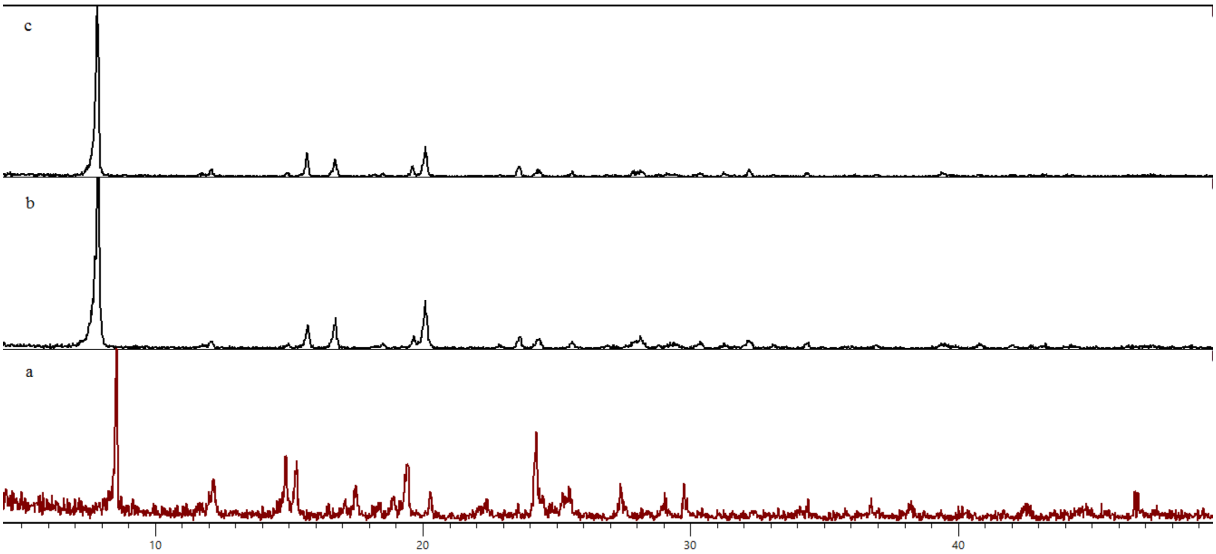

Figure D31. Compared diffractograms of **1a** (a); **1** from recrystalisation of **1a** in MeCN (b); **1** (c).

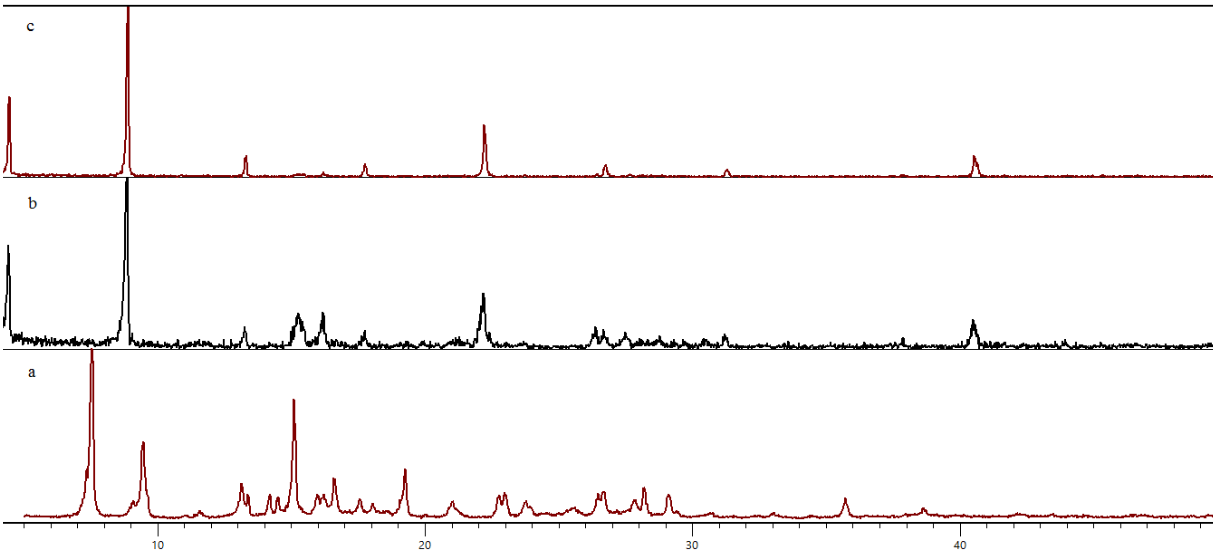

Figure D32. Compared diffractograms of **2a** (a); **2** from recrystalisation of **1a** in MeCN (b); **2×MeCN** (c).

§ 9. CURRICULUM VITAE

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