



DEPARTMENT OF PHYSICAL AND ANALYTICAL CHEMISTRY

**SYNTHESIS, REACTIVITY AND CATALYTIC ACTIVITY OF
Mo₃S₄ CLUSTERS CONTAINING CYCLIC AMINES.**

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Bachelor's Degree Final Project

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ABBREVIATIONS

acac	Acetylacetonate
Bu ₄ NCl	Tetrabutylammonium chloride
Cp*	Pentamethylcyclopentadienyl
¹³ C{ ¹ H}NMR	Carbon nuclear magnetic resonance
°C	Centigrade
<i>ca.</i>	Circa (approximately)
DPH	1,2-diphenylhydrazine
dmad	Dimethyl acetylenedicarboxylate
DMF	Dimethylformamide
dmen	N,N'-dimethylethylenediamine
dmpe	1,2-bis(dimethylphosphino)ethane
dnbpy	4,4'-dinonyl-2,2'-bipyridine
dpa	Diphenyl acetylene
dien	Diethylenetriamine
DFT	Density Functional Theory
δ	Chemical shift
ESI-MS	Electrospray Ionization Mass Spectrometry
Et	Ethyl
equiv.	Equivalents
exc	Excess
<i>et al.</i>	<i>Et alii</i> (and other authors)
Et ₂ O	Diethyl ether
FID	Flame Ionization Detector

GC	Gas Chromatography
g	Grams
h	Hour
HDF	Hydrodefluorination
HSQC	Heteronuclear Single Quantum Correlation
HER	Hydrogen Evolution Reaction
m/z	Mass to charge ratio
mL	Milliliter
min	Minute
MeOH	Methanol
mmol	Millimol
μL	Microliter
LC	Liquid Chromatography
nta	Nitrilotriacetic acid
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
py	Pyridine
nta	Nitrilotriacetic acid
r.t	Room temperature
tacn	1,4,7- triazacyclononane
UV-Vis	Ultraviolet-Visible spectroscopy

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1

INTRODUCTION

1. Introduction

1.1 General aspects

The term cluster was introduced in 1964 by F. A. Cotton to designate a finite group of metal atoms which are held together primarily, or at least to a significant extent, by direct bonds between metal atoms.¹ Nowadays, polynuclear transition metal clusters constitute a broad class of coordination compounds with applications in different fields such as molecular electronics, magnetism, luminescence, non-linear optics and catalysis.

Transition metal clusters can be classified according to the electronic nature of the metal into electronically rich and electronically poor. The former are constituted by transition metals located at the right side of the periodic table in low oxidation states and are bound to acceptor ligands such as carbonyls (CO), nitric oxide (NO), hydrides (H), phosphines (PR₃) and cyclopentadienyl (Cp). The most representative family of electronically rich complex clusters are the carbonyl ones. Some typical examples are shown in Figure 1.

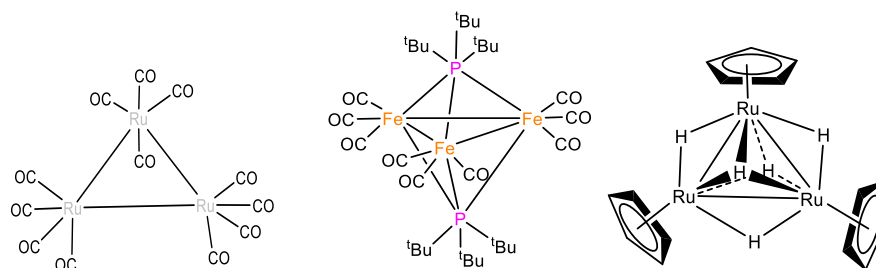


Figure 1. Representative examples of electron rich clusters

Electronically poor transition metal clusters are made up of transition metals located at the left side of the periodic table in high oxidation states. These metals generally bind electron-donating ligands such as halogens (Cl, Br, or I), oxygen (O²⁻), or chalcogens (S²⁻ or Se²⁻). The metallic skeleton of these clusters usually adopts triangular or octahedral geometries. Some typical examples are shown in Figure 2.

¹ Cotton, F. A. *Inorg. Chem.* **1964**, 3, 1217–1220.

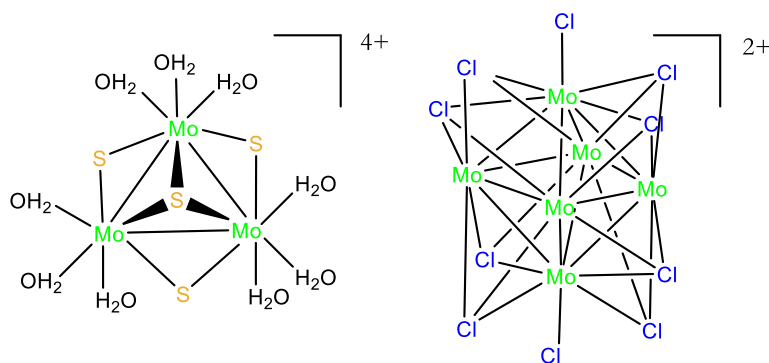


Figure 2. Representative examples of electron poor clusters.

In this Final Degree Project we will focus on electronically poor molybdenum sulfide Mo_3S_4 clusters. These complexes have a very robust structure due to the sulfide bridging ligands, so external ligands can be easily modified without interfering with the core structure complex. The three metals are linked by three bridging and one capping sulfur atoms. If we disregard metal-metal bonds, the metal has a distorted octahedral environment with three sulfur atoms and three terminal ligand donor atoms.

The molecular diagram of the Mo_3S_4 cluster unit is shown in Figure 3. According to this diagram the clusters are stable when the three bonding orbitals ($1a_1$ and $1e$) are filled, that is, each Mo(IV) atom provide two electrons with a total of six electrons for the formation of three metal-metal bonds.

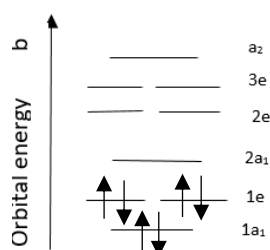
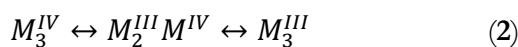
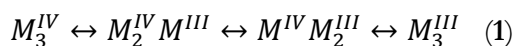


Figure 3. Orbital diagram Mo_3S_4 .

A typical feature of Mo_3S_4 clusters is the presence of either three successive one-electron reductions or successive two- and one- electron reductions, as is represented in equations 1 and 2. These processes depend directly on the nature of the terminal ligands and are accompanied by the occupation of the non-bonding ($2a_1$) and antibonding ($2e$) orbitals, respectively.²

² Nielsen, M.T.; Padilla R.; Nielsen, M. Homogeneous Catalysis by Organometallic Polynuclear Clusters. *Journal of Cluster Science*, **2019**.



Nowadays, a large number of Mo_3S_4 clusters have been isolated with ligands of different denticities: monodentate such as H_2O , PPh_3 , Cl , Br or bidentate ligands such as diamine, diphosphine or diimine. Finally, although less frequent, tridentate ligands which include ligands such as *tacn*, *dien* and *nta* among others. Typical examples of clusters structures incorporating mono-, bi- and tridentate ligands are illustrated in Figure 4.

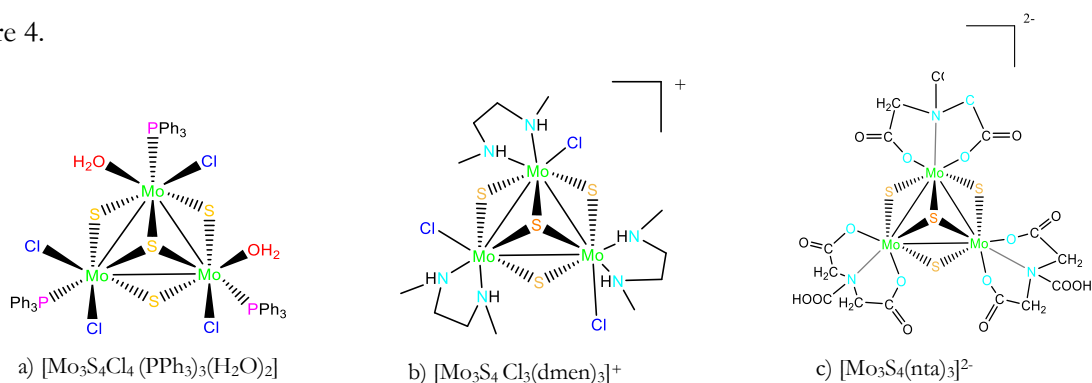


Figure 4. Typical examples of Mo_3S_4 containing a) mono-, b) bi-, and c) tridentated ligands

From structural point of view, transition metal Mo_3S_4 clusters have an incomplete cubane type structure, where the metal and chalcogen atoms occupy adjacent vertices in a cube with a missing metal atom. These trimetallic complexes have some characteristic reactivity features, such as the incorporation of a second metal atom to afford heterobimetallic $Mo_3M'S_4$ clusters or the insertion of alkyne molecules to give dithiolene adducts.

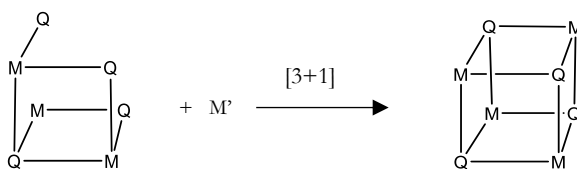
Cubane-type $Mo_3M'S_4$ complexes are usually prepared through a [3+1] synthetic strategy by adding a monomeric compound containing the M' metal to an incomplete cubane-type structure, this can be seen in scheme 1. Once the heterobimetallic compound has been formed, it can undergo different chemical transformations without changing the nuclearity.³ The formation of these heterobimetallic clusters has interesting applications in catalysis which depends on the nature of the metal M' .⁴

In the field of homogeneous catalysis there are a large number of applications of these complexes. Some Mo_3NiS_4 clusters can catalyze the intramolecular cyclization of terminal alkynoic acids to give enol

³ A. L. Gushchin, Y. A. Laricheva, M. N. Sokolov, and R. Llusar, "Tri- and tetranuclear molybdenum and tungsten chalcogenide clusters: on the way to new materials and catalysts," *Russ. Chem. Rev.*, **2018**, vol. 87, no. 7, pp. 670–706.

⁴ Seino, H.; Hidai, M. *Chemical Science* **2011**, *2*, 847-857.

lactones,⁵ also the polymerization reaction of methyl methacrylate and the decomposition of hydrazine to give ammonia and nitrogen are processes catalyzed by Mo_3RuS_4 unit clusters.⁶⁷



Scheme 1. Building-block synthetic methods for heterometallic cubane clusters.

Compounds with central $\text{M}_3\text{M}'\text{Q}_4$ cores exhibit simple, edge-joining double-cube, and corner-sharing double-cube structures, as depicted in Figure 5. In the case of the first-row transition heterometals, to date only the first two structural types have been found.⁸

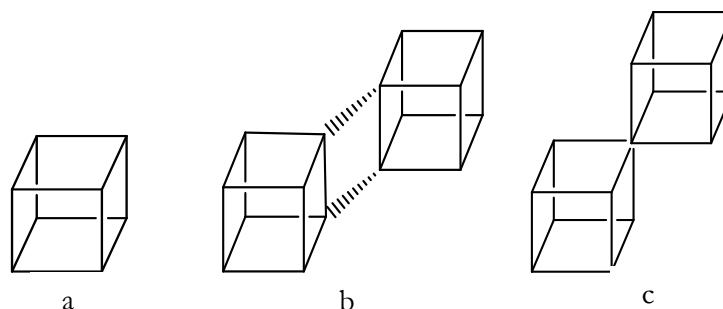


Figure 5. Structural types of $\text{M}_3\text{M}'\text{Q}_4$ aquo cuboidal clusters: a) single cubane b) edge-linked double cubane c) corner-shared double cubane.

The chemistry of heterodimetallic clusters with $\text{M}_3\text{M}'\text{Q}_4$ cores was first developed predominantly in aqueous media, and major advances have been made for molybdenum clusters, where the heterometals incorporated into the incomplete cuboidal $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ aquo range from group 6 to group 15. There have been important advances using organic solvents synthetic routes to obtain the $\text{M}_3\text{M}'\text{S}_4$ clusters with cyclopentadienyl ligands, phosphines, among others, in which CH_3CN , CH_2Cl_2 , EtOH have been used as reaction media.⁹

On the other hand, reaction of Mo_3S_4 clusters with alkynes leads to the formation of dithiolene derivative. This reactivity was initially reported by Shibahara *et al.* in 1993.¹⁰ The main interest of this type

⁵ Takei, I.; Wakebe, Y.; Suzuki, K.; Enta, Y.; Suzuki, T.; Mizobe, Y.; Hidai, M. *Organometallics*. **2003**, 22, 4639.

⁶ Seino, H.; Hidai, M. *Chem. Sci.* **2011**, 2, 847.

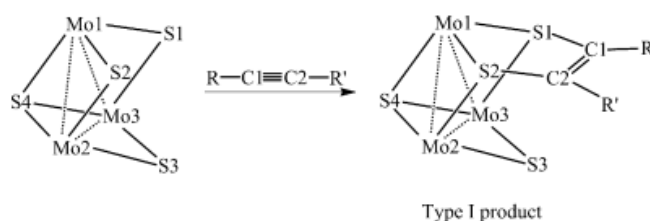
⁷ Takei, I.; Dohki, K.; Kobayashi, K.; Suzuki, T.; Hidai, M. *Inorg. Chem.* **2005**, 44, 3768.

⁸ Llusar, R. Uriel, S. *Eur. J. Inorg. Chem.* **2003**, 1271-1290.

⁹ Llusar, R. Uriel, S. *Eur. J. Inorg. Chem.* **2003**, 1271-12906.

¹⁰ Y. Ide, T. Shinahara, G. Sakane, S. Mochida. *J. Am. Chem. Soc.* **1993**, 115, 10408-10409.

of reaction lies in the formation of C-S bonds through the reaction of the bridging sulfur atoms with acetylene or its derivatives (scheme 2). This reaction occurs via a [3+2] cycloaddition and it is well known that the cycloaddition reaction between these complexes and alkynes is affected by the nature of the ancillary ligands on the complexes, as well as the alkyne substituents.



Scheme 2. Reaction between a Mo_3S_4 cluster and an alkyne

In 2018, the research group of Prof. Llusar reported the reaction between $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmen})_3]^+$ with *dmad*, giving rise to the formation of the corresponding dithiolene adduct, in which a characteristic band at 887 nm was observed by UV-Vis spectroscopy. The structure of the adduct was determined by single crystal X-ray diffraction, confirming the formation of two C-S bonds. The addition of the unsaturated molecule resulted in the loss of the C_{3v} symmetry of the incomplete Mo_3S_4 cuboidal precursor and also in the elongation of the two Mo-(μ -S) bonds involved in the dithiolene formation going from $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmen})_3]^+$ to $[\text{Mo}_3(\mu_3\text{-S})(\mu\text{-S})(\mu_3\text{-SC}(\text{CO}_2\text{CH}_3)=\text{C}(\text{CO}_2\text{CH}_3)\text{S})\text{Cl}_3(\text{dmen})_3]\text{BF}_4$ cluster.

The reaction of $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmen})_3]^+$ cluster with *dmad* involves an internal electron transfer process induced by the interaction with *dmad*, in which a bond shortening is observed between the Mo centers that do not participate in the [3+2] cycloaddition this is because the dithiolene adduct contains eight skeletal electrons that give the formation of two single Mo-Mo bonds and one double.^{11,12}

Regarding the catalytic activity, the Molecular Materials group has shown that Mo_3S_4 cluster sulfides are active in hydrodefluorination processes,^{13,14} photoinduced hydrogen evolution from water,¹⁵ the hydrogenation of nitro derivatives and the semihydrogenation of alkynes.¹⁶ In 2012, the same research group described that cubane-type hydrido Mo_3S_4 clusters functionalized with diphosphane ligands are

¹¹ A. G. Algarra *et al.*, "Cuboidal Mo_3S_4 Clusters as a Platform for Exploring Catalysis: A Three-Center Sulfur Mechanism for Alkyne Semihydrogenation," *ACS Catal.*, **2018**, vol. 8, no. 8, pp. 7346–7350.

¹² Young, C. G. Facets of early transition metal–sulfur chemistry: Metal–sulfur ligand redox, induced internal electron transfer, and the reactions of metal–sulfur complexes with alkynes. *J. Inorg. Biochem.* **2007**, 101, 1562–1585.

¹³ Beltrán, Tomás F.; Feliz, Marta; Llusar, Rosa; Mata, Jose A.; Safont, Vicent S. (2011). Mechanism of the Catalytic Hydrodefluorination of Pentafluoropyridine by Group Six Triangular Cluster Hydrides Containing Phosphines: A Combined Experimental and Theoretical Study. *Organometallics*, **2011**,30(2), 290–297.

¹⁴ Carmina, A.; Beltrán, T.F.; Feliz, M.; Llusar, R. Influence of the Diphosphine Coordinated to Molybdenum and Tungsten Triangular M_3S_4 Cluster Hydrides in the Catalytic Hydrodefluorination of Pentafluoropyridine. *Journal of Cluster Science*, **2015**, vol 26, no.1, 199–209.

¹⁵ Recatalá, D. *et al.* Photogeneration of Hydrogen from Water by Hybrid Molybdenum Sulfide Clusters Immobilized on Titania. *ChemSusChem*, **2015**, vol 8, no 1, p. 148–157.

¹⁶ Nielsen, M.T.; Padilla R.; Nielsen, M. Homogeneous Catalysis by Organometallic Polynuclear Clusters. *Journal of Cluster Science*, **2019**.

active for the selective transfer hydrogenation of nitroarenes in the presence of formate as reducing agents.¹⁷ The active sites in this case have been identified as the Mo-H bonds.

The same cluster unit decorated with diamine ligands has been used for the selective catalytic hydrosilylation of nitro- and azo compounds under mild conditions.¹⁸ Although both systems are attractive for the synthesis of specific anilines at laboratory scale, they suffer from low atom-efficiency. Later on, the group developed an environmentally friendlier catalytic protocol for the reduction of nitro- and azo compounds that makes use of molecular hydrogen, which is a cheap and “green” reducing agent.

In 2017, Llusar *et al.* reported the direct hydrogenation of aromatic nitro compounds catalyzed by well-defined Mo₃S₄ clusters bearing diimine and diamine ligands.¹⁹ In collaboration with Prof. Beller, a catalytic process for the synthesis of secondary amines has been developed applying a domino catalytic transformation starting from nitroarenes or nitroalkanes and aldehydes by direct hydrogenation using the above diamino cluster as catalysts.¹⁹ Amines represent a privileged class of chemicals, which are extensively used in organic synthesis while they are valuable intermediates for the manufacture of dyes, pigments, agrochemicals, and pharmaceuticals.

Later on, in collaboration with Basallote’s group the Molecular Materials group has extended the direct hydrogenation catalytic protocol to the semihydrogenation of alkynes using also the diamino Mo₃S₄ cluster as catalyst.²⁰ The reaction mechanism was elucidated by means of spectroscopic and spectrometric reaction monitoring guided by DFT calculations. This work demonstrated that H₂ activation occurs in an unprecedented way that involves one of the carbon atoms of the dithiolene-Mo₃S₄ adduct formed upon alkyne addition and the third bridging sulfur of the Mo₃S₄ unit, as illustrated in Figure 6(left). In 2021, Llusar and Basallote extended their work on catalytic direct hydrogenation to the selective conversion of azobenzene to aniline and they postulated an uncommon mechanism in which hydrogen activation occurs at the bridging sulfurs, represented in Figure 6(right).²¹

¹⁷ Sorribes, I.; Wienhöfer, G.; Vicent, C.; Junge, K.; Llusar, R.; Beller, M. Chemoselective Transfer Hydrogenation to Nitroarenes Mediated by Cubane-Type Mo₃S₄ Cluster Catalysts. *Int.Engl. Ed.* **2012**, 51, p.7794-7798.

¹⁸ Pedrajas, E.; Sorribes, I.; Junge, K.; Beller, M.; Llusar, R. A Mild and Chemoselective Reduction of Nitro and Azo Compounds Catalyzed by a Well-Defined Mo₃S₄ Cluster Bearing Diamine Ligands. *ChemCatChem*, **2015**, 7(17), p. 2675–2681.

¹⁹ Pedrajas, E.; Sorribes, I.; Junge, K.; Beller, M.; Llusar, R. Selective reductive amination of aldehydes from nitro compounds catalyzed by molybdenum sulfide clusters. *Green Chem.* **2017**, 19, p. 3764-3768.

²⁰ Algarra, A. G.; Guillamón, E.; Andrés, J.; Fernández-Trujillo, M. J.; Pedrajas, E.; Pino-Chamorro, J.A.; Llusar, R.; Basallote, M.G. Cuboidal Mo₃S₄ clusters as a platform for exploring catalysis: A three-center sulfur mechanism for alkyne semihydrogenation. *ACS Catalysis*. **2018**, 8, p.7346-7350.

²¹ Guillamón, E.; Oliva, M.; Andrés, J.; Llusar, R.; Pedrajas, E.; Safont, V.S.; Algarra, A.; Basallote, M. *ACS Catalysis*. **2021**, 11 (2), 608-614.

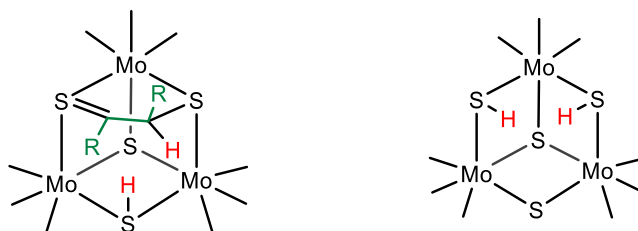


Figure 6. Hydrogen activation by Mo_3S_4 clusters: some representative intermediates.

The hydrogenation of azobenzene to aniline catalyzed by the $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmen})_3]^+$ cluster cation, represented in Figure 7, occurs through the formation of 1,2-diphenylhydrazine as a detectable intermediate. A mechanism was proposed in which the formation of 1,2-diphenylhydrazine and aniline occurs through two interconnected catalytic cycles that share a common reaction step involving the addition of H_2 to two of the catalyst's bridging sulfur atoms to form a dithiolate $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-SH})_2(\mu\text{-S})$ adduct.

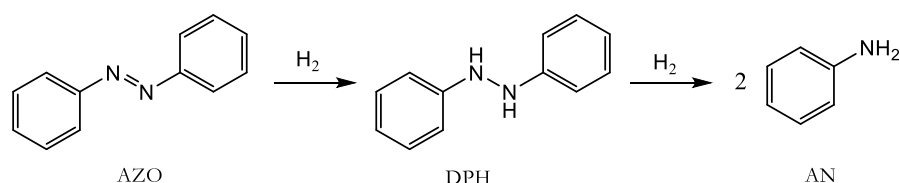


Figure 7. Sequential conversion of azobenzene to 1,2-diphenylhydrazine and aniline

Clusters with tridentated ligands such as $[\text{Mo}_3\text{S}_4(\text{tacn})_3]^{4+}$ are also active catalysts for the hydrogenation of azobenzene although conversions are much lower and required acidic conditions. Because the outer positions of each metal in this cluster catalyst are completed by a tridentate facially coordinated cyclic amine ligand, the formation of an active Mo-based reaction site is highly unlikely. This finding gives support to the above mentioned sulfur-based mechanism in which hydrogen activation occurs at the bridging sulfur ligands. On the other hand, this is the only example of an hydrogenation catalytic process mediated by Mo_3S_4 clusters in which acidic conditions are required and this work plans to investigate the influence of the pH on the catalytic activity of this tridentated cluster in the hydrogenation of azobenzene reaction.

The reactivity of Mo_3S_4 clusters containing tridentate ligands has received little attention. As previously mentioned, these clusters can react with a second transition metal to afford heterobimetallic $\text{Mo}_3\text{M}'\text{S}_4$ complexes and with alkynes to give dithiolene adducts. In this work the reactivity of

$[\text{Mo}_3\text{S}_4(\text{tacn})_3]^{4+}$ towards a second metal or an alkyne is also analyzed. Interestingly, alkyne addition is the first step of the semihydrogenation reaction catalyzed by this kind of clusters.

2

OBJECTIVES

In recent years, Mo_3S_4 clusters have attracted much interest due to their potential as catalysts in different processes. The properties of such clusters can be modulated by changing the external ligands. In fact, there are numerous examples of Mo_3S_4 clusters containing bidentate ligands in catalysis while the catalytic activity of Mo_3S_4 clusters containing tridentate ligands is almost unexplored. This work focusses on the catalytic activity and reactivity of Mo_3S_4 derivatives containing cyclic amines coordinated in a tridentate fashion.

The specific objectives of this work can be summarized in the following points:

- i) Synthesis and characterization of the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster.
- ii) Study of the catalytic activity of the synthesized cluster in the hydrogenation of azobenzene to aniline at different pHs.
- iii) Evaluation of the reactivity of the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster towards alkynes.
- iv) Reactivity study of the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster towards a second transition metal.

3

EXPERIMENTAL SECTION

3.1 General considerations

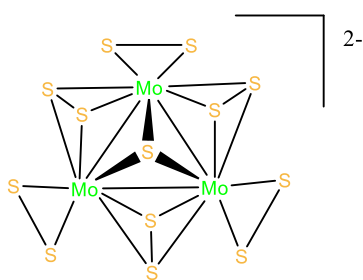
All reactions were carried out in an inert atmosphere using standard Schlenk techniques. Solvents used for synthesis were dried and degassed in a solvent purification system (SPS).

All the compounds prepared were characterized by spectroscopic and spectrometric techniques. Proton and carbon nuclear magnetic resonance were recorded on Bruker 300 and 400MHz Avance III HD spectrometer using D₂O as solvent. The electronic spectra have been obtained using an Agilent Cary 60 UV-Vis spectrophotometer. Electrospray ionization mass spectra (ESI-MS) were recorded with a Quattro LC unit (quadrupole-hexapole-quadrupole) using an octagonal Z-spray electrospray interface (MICromass, Manchester, UK). The composition of each peak has been assigned by comparing the experimental isotopic distribution with that calculated theoretically with the MassLynx 4.0 software.²² Finally, a gas chromatograph has been used to follow the degree of progress of the reduction of the azo compounds to the amine group and its quantification in an Agilent 7820A device equipped with a flame ionization detector (FID) and an HP-5 capillary column.

3.2 Starting materials

Precursor compounds have been synthesized and characterized following published procedures. Reactants were obtained from commercial sources and were stored in a safe way and used without further purification.

$(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}] \cdot n\text{H}_2\text{O}$ ($n = 0-2$)²³



Elemental sulfur (27 g, 0.84 mmol) was dissolved in 120 mL of (NH₄)₂S (20% purity) to obtain a reddish solution. Simultaneously, (NH₄)₆[Mo₇O₂₄]·4H₂O (4 g, 3.24mmol) was dissolved in 20 mL of water in a 250 mL Erlenmeyer flask and the resultant solution was warmed to 40°C. Then, the polysulfide solution was slowly added to the aqueous molybdate solution and the flask was covered with a watch glass. The

dark red mixture was kept at 82 – 85 °C for 5 days without stirring. After cooling to room temperature, a red microcrystalline solid appeared and was filtered. The product was thoroughly washed with water, ethanol, carbon disulfide and diethyl ether. Yield: 5.05 g (88 %).

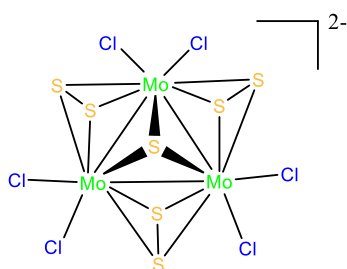
ESI(-)-(MS)(CH₃CN, 20 V): $m/z = 352$ [M]²⁻

²² MassLynx, 4.1 ed., Waters Corporation, Milford, Ma, 2005.

²³ Ginsberg, A. P. *Inorganic Syntheses*, Vol.27:Hoboken,NJ,USA, 1990.

Elemental analysis calc. for $\text{H}_8\text{Mo}_3\text{N}_2\text{S}_{13}\cdot\text{H}_2\text{O}$ (%): H, 1.33; N, 3.69; S, 54.93; Exp (%): H, 1.10; N, 3.35; S, 55.80.

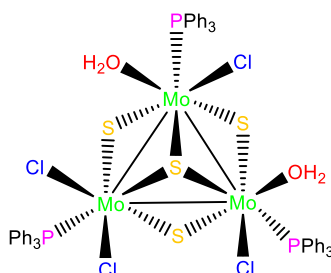
$(\text{Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7\text{Cl}_6]^{2-}$



A solution of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ (5 g, 6.59 mmol) in 250 mL of HCl (37% purity) was heated at 80 °C overnight under air. Precipitation of elemental sulfur was observed and was filtered off. Then, an excess of Bu_4NCl salt was added to the dark orange solution and left at 2°C for a few hours to afford complete precipitation. After this time, a microcrystalline orange solid appeared and was filtered and thoroughly washed with water, methanol and diethyl ether. Yield: 7.90 g (99 %).

ESI(-)-(MS)(CH_3CN , 20 V): $m/z = 362.7$ $[\text{M}]^{2-}$, 689 $[\text{M}-\text{Cl}]^{-}$

$[\text{Mo}_3\text{S}_4\text{Cl}_4(\text{PPh}_3)_3(\text{H}_2\text{O})_2]^{25}$

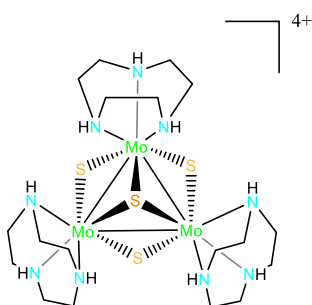


An excess of triphenylphosphine (0.321 g, 1.224 mmol) was added to a solution of $(\text{Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7\text{Cl}_6]$ (0.200 g, 0.165 mmol) in 5 mL of MeOH. After stirring for 25 min, the formation of a green suspension was observed. Finally, the green solid was filtered and washed with MeOH, a cold mixture of hexane/ toluene (1:1, v/v) and boiling hexane. Yield: 0.203 g (89%).

$^{31}\text{P}\{^1\text{H}\}$ RMN(CD_3CN , 121 MHz) δ (ppm) = 28.17; 24.41; -4.4 (PPh_3 free)

²⁴ V. P. Fedin, M. N. Sokolov, Y. V. Mironov, B. A. Kolesov, S. V. Tkchev, V. Y. Fedorov. *Inorganica Chim. Acta.* **1990**, 167, 39-45.

²⁵ M. Sasaki, G. Sakane, T. Ouchi, T. Shibahara, *J. Clust. Sci.* **1998**, 9, 25-43.

[Mo₃S₄(tacn)₃]Cl₄²⁶

A solution containing an excess of tacn (100 mg, 0.77 mmol) in 1 mL of DMF previously bubbled with N₂, is added to a solution of [Mo₃S₄Cl₄(PPh₃)₃(H₂O)₂] (71.2 mg, 0.051 mmol) in 7 mL of DMF. After refluxing the reaction mixture for 4 h, it is allowed to cool to room temperature to afford a suspension. Finally, the solid was separated by filtration and washed with DMF, hot hexane and Et₂O obtaining the desired green solid. Yield: 37 mg (76%)

ESI-(+)-(MS)(H₂O, 20 V): m/z = 268 [M]³⁺, m/z = 400 [M]²⁺, ¹H-NMR (D₂O): 2.94-2.97(m, 2H, -NCH₂-), 3.08-3.14(m, 2H, -NCHH-), 3.16-3.5 (m, 20H, -NCHH-HHCN-), 3.67-3.76(d, 4H, -NCHH-HHCN), 3.88-3.96(m, 4H, -NCHH-HHCN-), 3.67-3.76(m, 4H, -NCHH-HHCN-).

3.3 Reactivity of [Mo₃S₄(tacn)₃]Cl₄ cluster**3.3.1 Reaction vs alkynes****Reaction of [Mo₃S₄(tacn)₃]Cl₄ with diphenylacetylene**

To a solution of diphenylacetylene (8.911 mg, 0.05 mmol) in 2.5 mL ACN is added a solution of [Mo₃S₄(tacn)₃]Cl₄ (4.747 mg, 5x10⁻³ mmol) in 5 mL of MeOH and the resulting mixture is stirred for 24 hours at room temperature. After this time, formation of the cluster adduct is evaluated by UV-Vis and ESI-MS measurements.

Reaction of [Mo₃S₄(tacn)₃]Cl₄ with phenylacetylene

To a solution of phenylacetylene (5.096 mg, 0.05 mmol) in 2.5 mL ACN is added a solution of [Mo₃S₄(tacn)₃]Cl₄ (4.747 mg, 5x10⁻³ mmol) in 5 mL of MeOH and the resulting mixture is stirred for 24 hours at room temperature. After this time, formation of the cluster adduct is evaluated by UV-Vis and ESI-MS measurements.

Reaction of [Mo₃S₄(tacn)₃]Cl₄ with dimethyl acetylenedicarboxylate

To a solution of dimethyl acetylenedicarboxylate (7.091 mg, 0.05 mmol) in 2.5 mL ACN is added a solution of [Mo₃S₄(tacn)₃]Cl₄ (4.747 mg, 5x10⁻³ mmol) in 5 mL of MeOH and the resulting mixture is stirred for 24 hours at room temperature. After this time, formation of the cluster adduct is evaluated by UV-Vis and ESI-MS measurements.

²⁶ Guillaón, E.; Oliva, M.; Andrés, J.; Llusar, R.; Pedrajas, E.; Safont, V. S.; Algarra, A.; Basallote, M. *ACS Catalysis* **2021**, *11* (2), 608-614

3.3.2 Reactivity vs Cu and Pt

Reaction of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ with CuCl

An excess of CuCl (5.24 mg, 0.053 mmol) was weighed into the dry box and dissolved in 2.5 mL of ACN. The resulting solutions was added to a solution of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ (10 mg, 0.077 mmol) in 5 mL of dry MeOH. After five minutes the color of the reaction mixture changed from green to red-brownish. The mixture was allowed to react for 24h and then analyzed by UV-VIS spectroscopy and ESI-MS measurements.

Reaction of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ with Pt(PPh_3)₄

An excess of Pt(PPh_3)₄ (26.85mg, 0.021 mmol) was weighed into the dry box and dissolved in 2.5 mL of ACN. The resulting solutions was added to a solution of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ (10 mg, 0.077 mmol) in 5 mL of dry MeOH. No color changes was appreciated so the mixture was allowed to react for 24h and then analyzed by UV-VIS spectroscopy and ESI-MS measurements.

3.4 Catalytic activity test.

Catalytic tests were performed using H₂ as reducing agent in 4 mL vials. Azobenzene (18 mg, 0.1 mmol), n-hexadecane (15 μl ; used as internal standard), and 5mol% of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ catalyst (4.72 mg) were mixed in the vials and dissolved in 2 mL of MeOH at different pH.²⁷

To adjust the pH of the MeOH solutions, HBF₄·Et₂O was used for pH 2 and 4. Neat MeOH was used for pH 6 and triethylamine was used to reach pH 8. Then, the vials were placed on a magnetic stirrer and closed with a septum pierced with a syringe needle and introduced into the sample holder of the autoclave reactor, which was hermetically sealed. Following, H₂ pressure was adjusted to 15 bar and the reactor was left at 70°C for 18h. Finally, the reactor is allowed to cool for approximately 10 minutes and depressurized. Then 2 mL of ethyl acetate is added to each of the vials and an aliquot is filtered to analyze the filtrate by GC. All reactions were replicated at least twice.

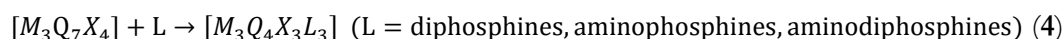
²⁷ Guillamón, E.; Oliva, M.; Andrés, J.; Llusar, R.; Pedrajas, E.; Safont, V. S.; Algarra, A.; Basallote, M. *ACS Catalysis* 2021 11 (2), 608-614.

4

RESULTS AND DISCUSSION

4.1 Synthesis and characterization of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster.

The synthesis and isolation of M_3Q_4 (M=Mo, W and Q=S, Se) clusters has undergone a great development along the years. Originally, non-rational methods namely bottom-up strategies were used to afford the trimetallic units starting from fragments of lower nuclearity. Subsequently, a more rational synthetic method was developed in the 1980s. This methodology was based on the excision of $[\text{M}_3\text{Q}_7\text{X}_4]_n$ (X=Cl, Br) polymeric phases according to equation 4. Through this synthetic route Llusar *et al.* have prepared a wide family of trinuclear cluster compounds coordinated to diphosphines, aminophosphines, aminodiphosphines.²⁸



This reaction takes place in the presence of desulfurizing agents such as phosphines capable of reducing the dichalcogenide bridges, giving rise to the M_3Q_4 cluster core. However, when diimino and/or diamino ligands are used to carry out the excision reaction, it takes place in low yields. Therefore, it is necessary to choose another synthetic route to synthesize such clusters and, by extension, the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster presented in this work.

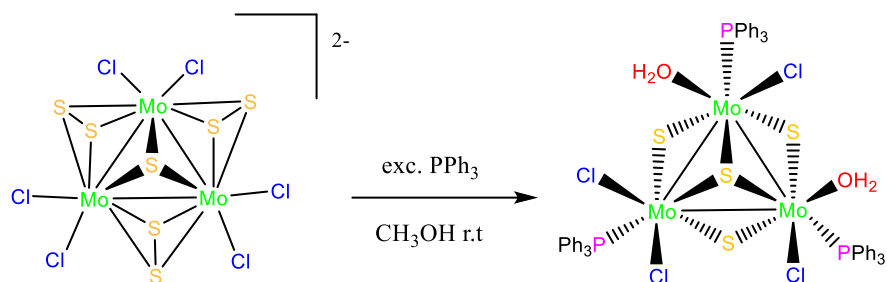
The first synthesis reported to prepare the cluster used in this work was published by F.A.Cotton in 1986,²⁹ where the crystal structure could be obtained in acid medium. The authors were able to isolate the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]^{4+}$ cluster by reacting the cubane-type tetrametallic $\text{Mo}_4\text{S}_4(\text{NCS})_{12}$ with 1,4,7-triazacyclononane trihydrobromide under inert atmosphere for 24h and leaving it to crystallize in a strong acid solution.

Recently, Llusar *et al.* have published an improved strategy to prepare the same cluster. This methodology has been used in this work and uses the $[\text{Mo}_3\text{S}_7\text{X}_6]^{2-}$ anionic cluster as starting material. The $[\text{Mo}_3\text{S}_7\text{X}_6]^{2-}$ complex is reacted with an excess of a cheap phosphine, namely triphenylphosphine. The driving force of this reaction is the formation of S=P bonds, thus obtaining the $[\text{Mo}_3\text{S}_4(\text{PPh}_3)_3\text{Cl}_4(\text{H}_2\text{O})_2]$ cluster with more labile ligands, as represented in scheme 4.³⁰

²⁸ T. F. Beltrán, J. Á. Pino-Chamorro, M. J. Fernández-Trujillo, V. S. Safont, M. G. Basallote, R. Llusar, *Inorg. Chem.* **2015**, *54*, 607–618.

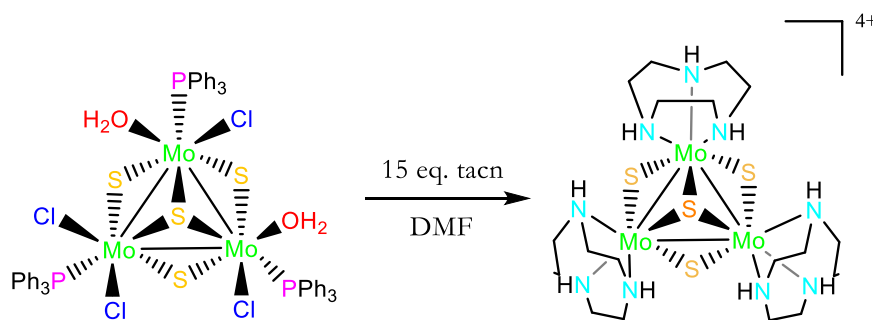
²⁹ Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. Oxidative fragmentation of the cuboid molybdenum-sulfur Mo_4S_4 cluster core: synthesis and structures of $[\text{Mo}_3(\mu\text{-S})(\mu\text{-S})_3(\text{tacn})_3]^{4+}$ and $\{\text{MoO}(\text{tacn})_2(\mu\text{-S})_2\}^{2+}$ ($\text{tacn} = 1,4,7\text{-triazacyclononane}$). *Inorg. Chem.* **1986**, *25*, 3654–3658.

³⁰ Rosa Llusar; Santiago Uriel. *Heterodimetallic Chalcogen-Bridged Cubane-Type Clusters of Molybdenum and Tungsten Containing First-Row Transition Metals.* **2003**, *7*, 1271–1290. doi:10.1002/ejic.200390164.



Scheme 4. Synthetic route to obtain [Mo₃S₄(PPh₃)₃Cl₄(H₂O)₂] cluster.

The external ligands in the neutral [Mo₃S₄(PPh₃)₃Cl₄(H₂O)₂] precursor are easier to replace by diamine or diimine ligands. In fact, the desired [Mo₃S₄(tacn)₃Cl₄] cluster is obtained by refluxing the resulting [Mo₃S₄(PPh₃)₃Cl₄(H₂O)₂] cluster with a high excess of tacn in DMF for 4 hours (Scheme 5). The product precipitates in the reaction mixture and is isolated after filtering off the green solid and washing with DMF, hot hexane and Et₂O achieving a reaction yield of 76%.



Scheme 5. Synthetic route to obtain [Mo₃S₄(tacn)₃]Cl₄ cluster.

Characterization of the product was carried out by mass spectrometry (ESI-MS) and proton magnetic resonance spectroscopy (¹H-NMR). Both techniques have proven to be very useful to characterize these Mo₃S₄ clusters. The mass spectrum of [Mo₃S₄(tacn)₃]Cl₄, represented in Figure 7, shows two peaks: one centered at m/z= 268 and the other at m/z=401, associated to [M]⁺³ and [M]⁺², respectively. The experimental spectrum of the peaks [M]⁺³ and [M]⁺² match perfectly with the calculated isotopic pattern.

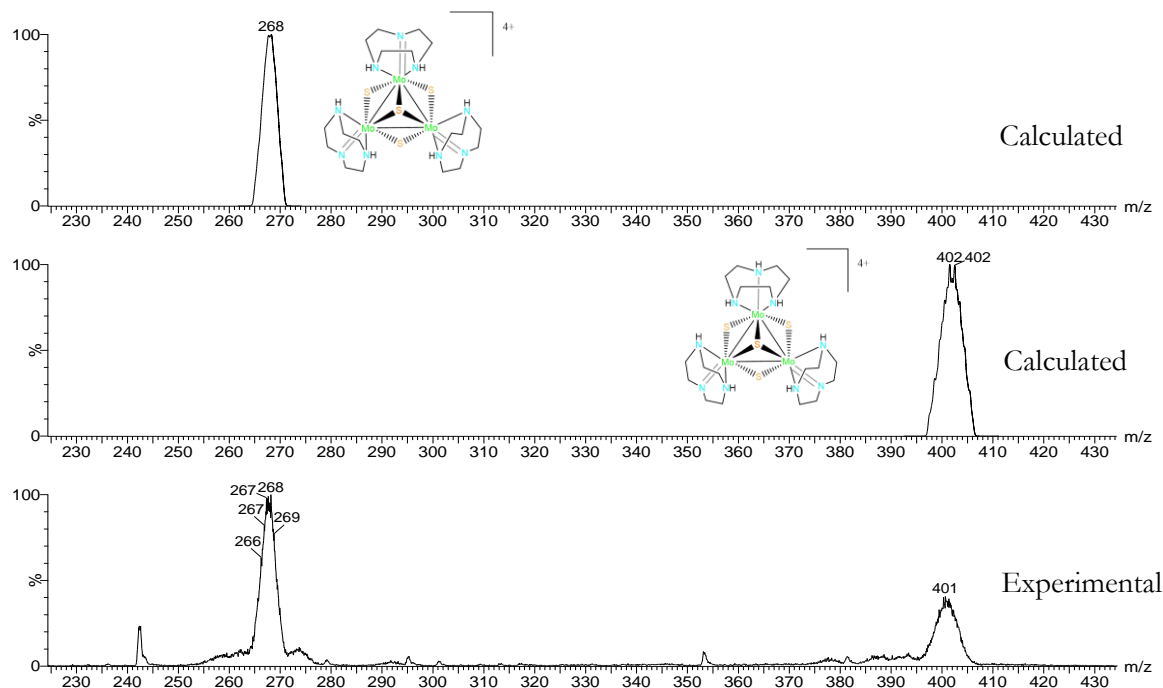


Figure 7. Experimental ESI-MS spectrum for the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]^{4+}$ cluster (bottom) and calculated spectra for the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]^{3+}$ and $[\text{Mo}_3\text{S}_4(\text{tacn})_3]^{2+}$ species (middle and up, respectively).

The $^1\text{H-NMR}$ spectrum reported by Llusar *et al.* for this compound was recorded in acidic D_2O medium (Figure 8, up). To our surprise, the spectrum of the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster recorded in this work in neutral D_2O medium revealed two additional triplets (Figure 8, bottom).³¹

³¹ Guillamón, E.; Oliva, M.; Andrés, J.; Llusar, R.; Pedrajas, E.; Safont, V. S.; Algarra, A.; Basallote, M. *ACS Catalysis* **2021**, *11* (2), 608-614.

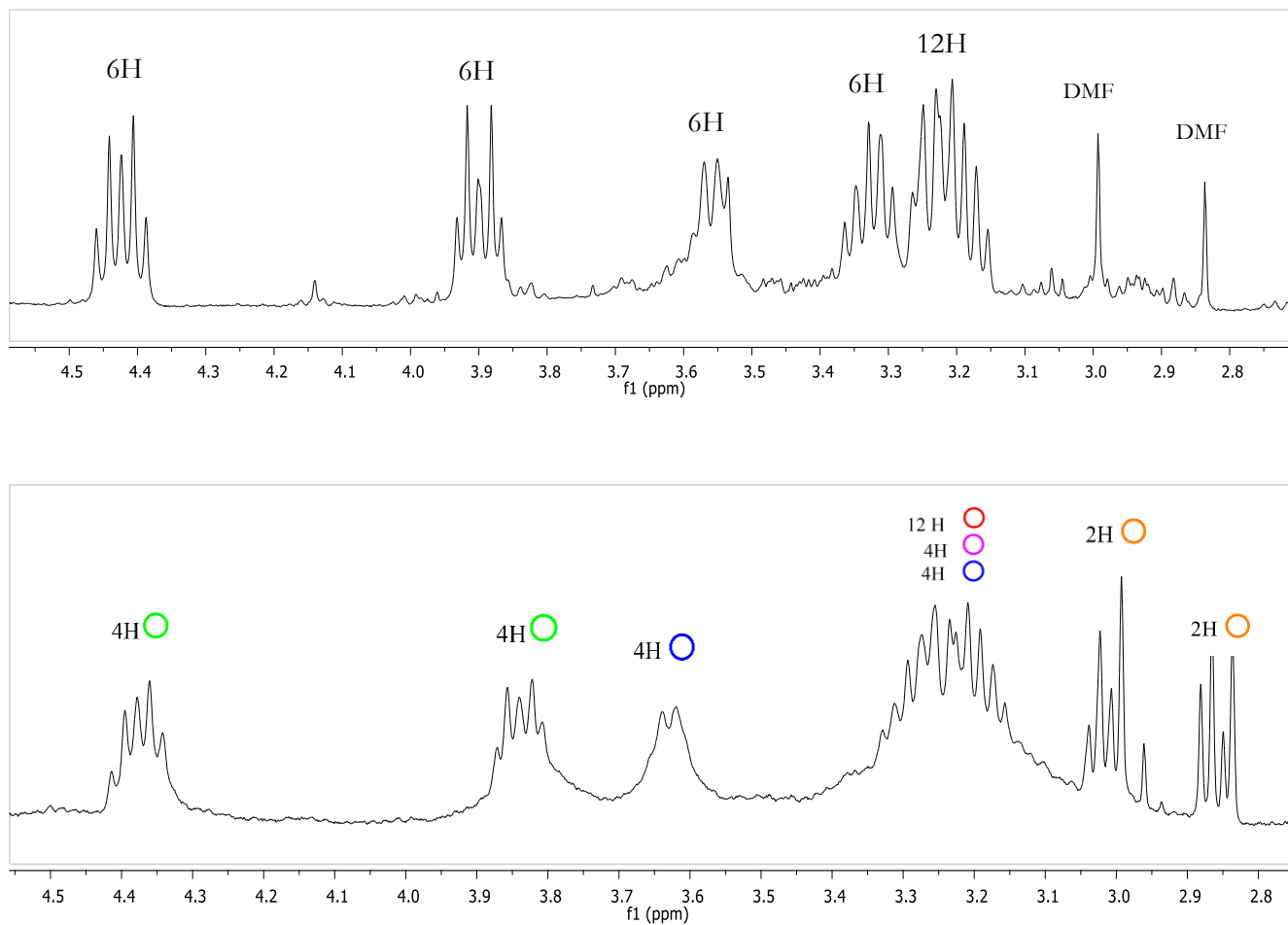


Figure 8. ^1H -NMR spectrum of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ compound in acidic medium(up) and in neutral medium(bottom)

The analysis of the spectrum obtained, led us to develop the following hypothesis. Due to the neutral medium, a deprotonation of an amine of the tacn ligand could occur. This hypothetical unsaturation in one of the amine group of the tacn ligand causes a difference between the Mo atoms, showing two different environments around the metallic centers, represented in Figure 9.

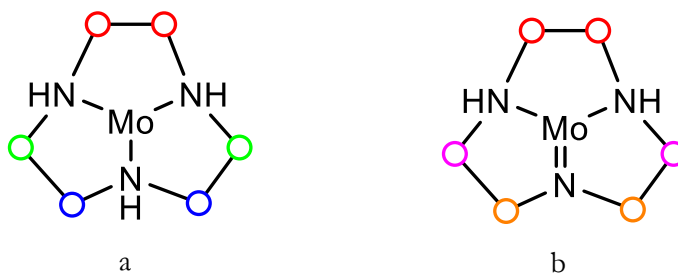


Figure 9. Hypothetical structure of the tacn ligand with one a) protonated and b) deprotonated nitrogen atom.

It can be observed that in such situation there should be 5 different hydrogen atoms, represented in colours in Figure 10. This hypothesis is based on the integral values of the ^1H NMR spectrum and is supported by the HSQC-NMR spectrum, shown in Figure 10.

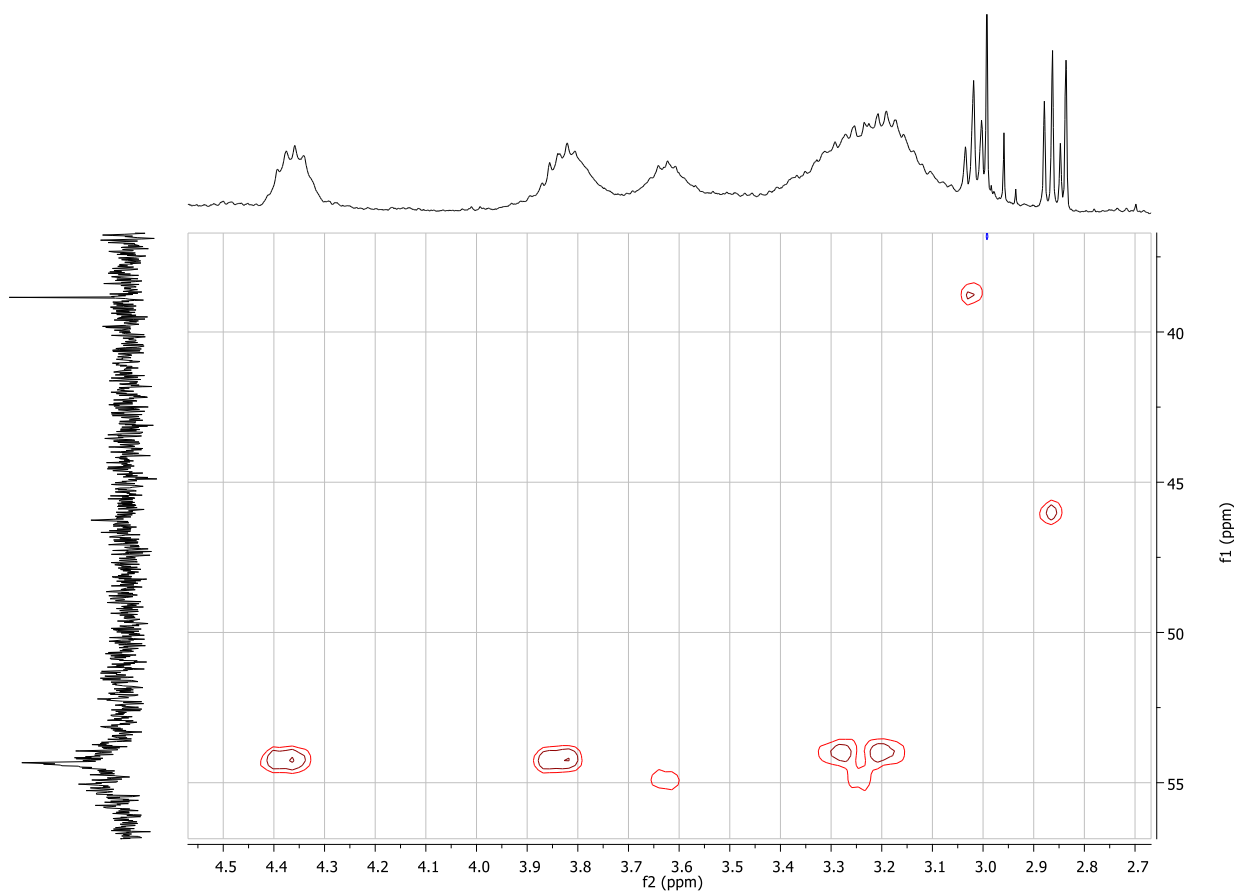


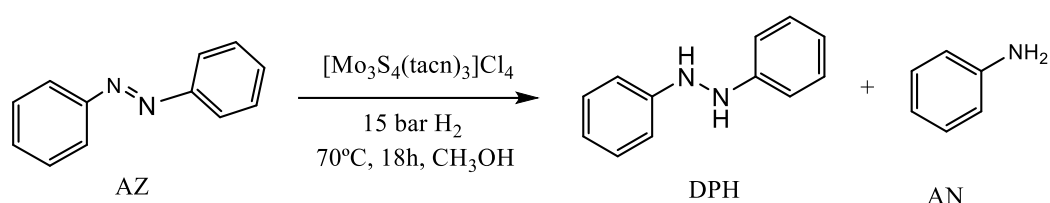
Figure 10. HSQC-NMR spectrum of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ compound in D_2O .

It can be observed that there is a broad signal at 54ppm associated to three different carbon atoms. Each carbon peak is coupled with two different proton signals indicating the diastereotopicity of such hydrogen atoms. On the other hand, the two triplet signals in the ^1H NMR are coupled with two different signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, indicating the loss of the diastereotopicity. Although these experiments gives support our hypothesis, further experiments should be carried out to unequivocally prove it.

4.2 Study of the catalytic activity of the synthesized cluster in the reduction of azobenzene to aniline and its influence at different pH.

The catalytic activity of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster in the reduction of azobenzene to aniline at different pH values has been investigated. Methanolic solutions were adjusted with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ to pH 2 and 4 and Et_3N was added to adjust pH to 8. To compare the catalytic results, reaction conditions were kept identical for each pH value. Originally, the experiment carried out by Llusar *et al.* in 2021 used conditions of 10 bar of H_2 pressure, 60 °C and 6 h. However, moderate yields were obtained. So in this work it was decided to harden the conditions to 15 bar of H_2 pressure, 70 °C and 18 h to optimize the results, which are shown in Table 1.

Table 1. Results for the reduction reaction of azobenzene to aniline at different pHs.^[a]



Entry	pH	Conversion (%) ^[b]	Yield (%) ^[b]	
			DPH	AN
1	2	51	14	19
2	4	28	9	11
3	6	34	11	13
4	8	33	10	13

[a] Reaction conditions: azobenzene (0.1 mmol), $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ catalyst (5 mol%), CH_3OH (2 mL). [b] Determined by GC analysis using n-hexadecane (15 μL) as an internal standard.

As expected, the best result was reached at the more acidic conditions although conversion was only moderate (see entry 1, Table 1). At higher pH, the reaction takes place with discrete conversion values as can be observed in entries 2-4 in table 1. The lower conversion at pH 4 (Table 1, entry 2) can be associated with experimental errors. Although it was expected a gradual decrease of the catalytic activity with increasing the pH, it can be concluded from the results in Table 1 that the catalyst needs strong acidic pH to catalyze the organic transformation.

On the other hand, Llusar *et al.* have investigated the role of the substituents on the N atom of bidentate ligands. They have proved that the catalytic activity of the cluster decreases or even disappears

when more substituted is the N atom in the ligand. This observation is in agreement with our results since at more basic pH, more probable of having the insaturated amine groups in tacn ligand, and subsequently more inactive becomes the catalyst.

4.3 Reactivity of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster vs Cu and Pt

As mentioned in the introduction section, such cubane-type trimetallic cluster has the ability to incorporate M' to give $\text{Mo}_3\text{M}'\text{S}_4$ complexes via the [3+1] synthesis route. For this reason we decided to study the reactivity of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster towards Cu and Pt.

The trinuclear $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster was reacted with CuCl for 24h at room temperature. The reaction proceeds with a color change from green to red-brownish typical of complex with a Mo_3CuS_4 core. The ESI-MS spectrum recorded at 0 and 20 V show a peak at $m/z = 268$ for $[\text{M}]^{3+}$ and $m/z = 400$ for $[\text{M}]^{2+}$ associated to the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cation. Therefore, we cannot confirm the formation of the corresponding Mo_3Cu derivative

The trinuclear $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster was also reacted with $\text{Pt}(\text{PPh}_3)_4$ for 24h, but no color change was observed. In addition the ESI-MS spectrum does not show the formation of a Mo_3Pt heterobimetallic complex. All attempts to characterize the heterobimetallic compounds by ESI-MS were unsuccessful. This can be explained because when the sample solutions are introduced in the equipment, they are applied a cone voltage is applied that could cause the loss of the heterometallic fragment what has been observed previously for other analogous heterobimetallic clusters.

4.4 Reactivity of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster alkynes

We also wanted to study the reactivity of the cluster towards alkynes of different nature, i.e., internal or terminal alkynes with electron donor or electron withdrawing substituents. The strategy is based on the [3+2] cycloaddition reaction which affords the dithiolate resulting product. The formation of this derivative can be evidenced by the UV-Vis analysis because the resulting dithiolate ligand shows a typical band in the 800-900nm region. After reacting the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ with a huge excess of the alkyne molecule for 24 h, the UV-Vis spectrum was recorded, all of them represented in Figure 11.

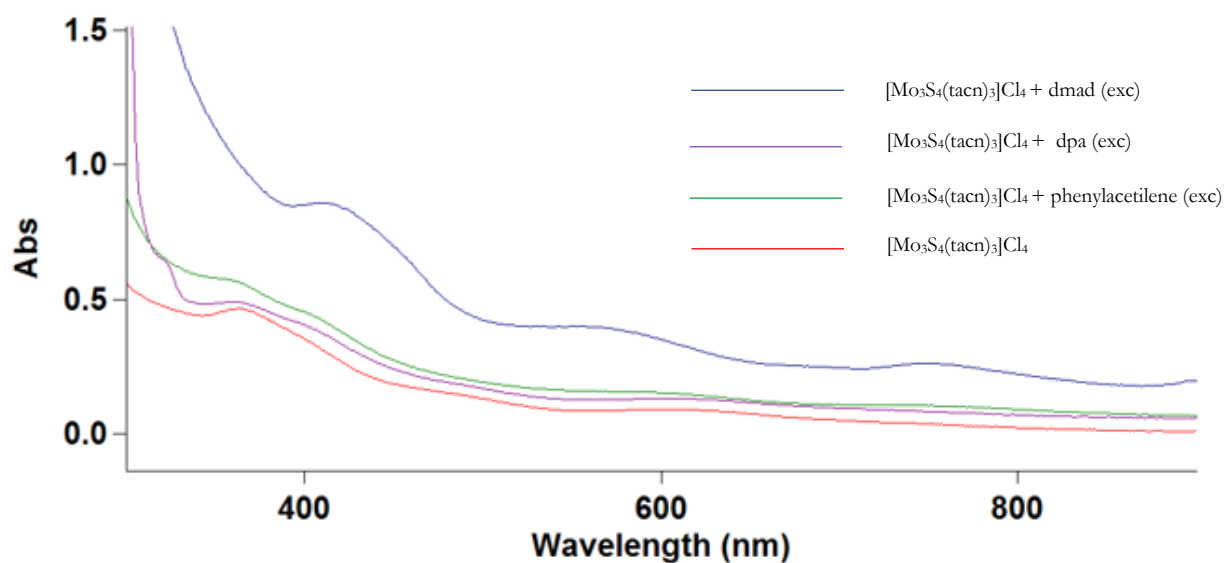


Figure 11. UV-Vis spectrum of absorption of the reactivity of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ towards alkynes.

By analysing the characteristic region for the dithiolate ligand, it is noteworthy that there is no noticeable changes. The only alkyne that causes tiny differences in the spectrum when compared with the cluster precursor is that for the dmad, although the formation of the adduct could not be confirmed by UV-Vis spectroscopy. So, the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster presents a poor reactivity towards this type of alkynes.

5

CONCLUSIONS

The experimental results obtained in this Bachelor's degree final project have allowed us to extract the following conclusions:

- i) Substitution of the outer ligands in the $[\text{Mo}_3\text{S}_4\text{Cl}_4(\text{PPh}_3)_3(\text{H}_2\text{O})_2]$ neutral cluster by tacn is an efficient method to synthesize the $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster in moderate yields.
- ii) Characterization of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster was carried out by mass spectrometry (ESI-MS) and proton magnetic resonance spectroscopy ($^1\text{H-NMR}$) techniques showing its sensitivity to the pH.
- iii) The activity of $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ as a catalyst for the reduction of azobenzene to aniline has been proven under highly acidic pH conditions although conversions and yield are only moderate.
- iv) The building block strategy [3+1] for the formation of heterobimetallic clusters of unit $\text{Mo}_3\text{M}'\text{S}_4$ ($\text{M}' = \text{Cu}$ or Pt) has been performed successfully.
- v) The trinuclear $[\text{Mo}_3\text{S}_4(\text{tacn})_3]\text{Cl}_4$ cluster has shown low reactivity towards different types of alkynes, being discrete only with dmad, an electron-poor alkyne.

