

**“BABES-BOLYAI” UNIVERSITY  
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING**

**SUPRAMOLECULAR ARCHITECTURES BASED ON  
POLYOXOMETALATE / MOLYBDENUM-OXIDE CLUSTERS**

*PhD Thesis  
ABSTRACT*

**Julia SZAKÁCS**

Scientific advisor:  
**Prof. Dr. Mariana RUSU**

**Cluj-Napoca  
2010**

**“BABES-BOLYAI” UNIVERSITY**  
**FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING**  
**Inorganic Chemistry Department**

**SUPRAMOLECULAR ARCHITECTURES BASED ON**  
**POLYOXOMETALATE / MOLYBDENUM-OXIDE CLUSTERS**

*PhD Thesis*  
*ABSTRACT*

**Julia SZAKÁCS**

Scientific advisor:  
**Prof. Dr. Mariana RUSU**

JURY:

**PRESIDENT**

Conf. Dr. Cornelia Majdik-Faculty of Chemistry and Chemical Engineering, “BABES-BOLYAI” University, Cluj-Napoca

**REVIEWERS**

Prof. Dr. Mircea Palamaru, University of “A.I.Cuza”, Iasi  
Prof. Dr. Lelia Ciontea, Technical University, Cluj-Napoca  
Conf. Dr. Edit F6rizs, University of “Babes-Bolyai”, Cluj-Napoca

**Cluj-Napoca**  
**2010**

## Table of Contents

Aknowledgements	10
List of compounds described in this dissertation	11
Chapter 1	
Theoretical background of the polyoxomolybdate chemistry	14
Theoretical background of the polyoxomolybdate chemistry	
1.1 Historical perspective	16
1.2 Methods of investigation of polyoxometalate anions in solid state and solution	18
1.2.1 Electronic spectroscopy	19
1.2.2 Vibrational spectroscopy	19
1.2.3 Equilibrium analyses	20
1.2.4 Nuclear Magnetic resonance (NMR)	21
1.2.5 Cerimetric titration	22
1.2.6 Single crystal X-ray measurement	22
1.2.7 Static and Dynamic Laser Light Scattering	23
1.3 Heteropolyoxometalates	23
1.4 Isopolyoxometalates: Polyoxomolybdates	26
1.4.1 Definition	26
1.4.2 The growth-principle	27
1.5 Structures and characteristics of some polyoxomolybdate clusters	31
1.5.1 The spherical type polyoxomolybdate clusters	32
1.5.2 The ring shaped molecular polyoxomolybdate clusters	34
1.5.2.1 {M <sub>O154</sub> } type wheel cluster	35
1.5.2.2 {M <sub>O176</sub> } type wheel cluster	36
1.5.2.3 The properties of giant ring shaped cluster units	36
1.5.3 Combined/hybrid type giant polyoxomolybdates	37
1.5.3.1 {M <sub>O248</sub> } type hybrid cluster	37

### 1.5.3.2 {Mo<sub>368</sub>} hybrid type cluster 39

#### Chapter 2

#### A Unique Metal-Oxide Based Reduced Hybrid: Core-Shell Electron Transfer upon Encapsulation 41

##### 2.1 Introduction 41

##### 2.2 Syntheses and the characterization of compounds 5-7 42

##### 2.3 Synthesis and characterization of

[H<sub>x</sub>P<sub>12</sub>Mo<sub>12</sub>O<sub>40</sub>⊂H<sub>4</sub>Mo<sup>VI</sup><sub>72</sub>Fe<sup>III</sup><sub>30</sub>O<sub>254</sub>(H<sub>2</sub>O)<sub>98</sub>(CH<sub>3</sub>COO)<sub>15</sub>]·ca.60H<sub>2</sub>O ≡ 4 (60; 63) 42

##### 2.4 Synthesis and characterization of Na<sub>4</sub>[SiMo<sub>12</sub>O<sub>40</sub>⊂H<sub>4</sub>Mo<sup>VI</sup><sub>70</sub>

Mo<sup>V</sup><sub>2</sub>Fe<sub>30</sub>O<sub>252</sub>(H<sub>2</sub>O)<sub>98</sub>(CH<sub>3</sub>COO)<sub>16</sub>] · ca. 60H<sub>2</sub>O ≡ 5 43

##### 2.4.1 Synthesis of the non-reduced hybrid compound 5C 43

##### 2.5 Synthesis and characterization of

[AsMo<sub>12</sub>O<sub>40</sub>⊂H<sub>4</sub>Mo<sup>VI</sup><sub>72</sub>Fe<sup>III</sup><sub>30</sub>O<sub>252</sub>(H<sub>2</sub>O)<sub>98</sub>(CH<sub>3</sub>COO)<sub>15</sub>] · ca. 60H<sub>2</sub>O ≡ 6 44

##### 2.6 Synthesis and characterization of

[HPW<sup>VI</sup><sub>11</sub>W<sup>V</sup>O<sub>40</sub>⊂Mo<sup>VI</sup><sub>65</sub>W<sup>VI</sup><sub>7</sub>Fe<sup>III</sup><sub>30</sub>(CH<sub>3</sub>COO)<sub>15</sub>O<sub>252</sub>(H<sub>2</sub>O)<sub>98</sub>]·ca.120H<sub>2</sub>O ≡ 7 44

##### 2.7 Different synthetical routes to achieve “host-guest” type chemistry 45

##### 2.8 Structural properties of the host-guest compounds 46

##### 2.9 Characteristic vibrational spectroscopy for the compounds 5 – 7 47

##### 2.10 <sup>57</sup>Fe Mössbauer spectroscopy 50

##### 2.11 Matrix-assisted laser desorption/ionization (MALDI-TOF) measurements 52

##### 2.12 Electronic absorption spectrum of compound 5 54

2.12.1 Spectroscopical investigations of the higher reduced species of the hybrid type compound containing silicomolybdic acid 55

##### 2.13 Determination of the number of reduced electrons in the host-guest type cluster 59

##### 2.14 Raman spectroscopical investigation 61

##### 2.15 Magnetic studies of the hybrid compound 5 64

##### 2.16 Conclusions and perspectives 65

## Chapter 3

Molybdenum-Oxide Based Unique Nanoacid of the Type  $\{\text{Mo}_{72}\text{Fe}_{30}\}$   
Showing Deprotonation and Interaction with Alkali Earth Metal Cations  
67

3.1 Introduction 67

3.2 Synthesis and characterization of  
 $\text{Ba}_5[\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}\text{O}_{252}(\text{CH}_3\text{COO})_{15}\{\text{Mo}_2\text{O}_7(\text{H}_2\text{O})\}_2\{\text{Mo}_2\text{O}_8(\text{H}_2\text{O})\}(\text{OH})_{10}(\text{H}_2\text{O})_8$   
 $]\cdot\text{ca.}150\text{H}_2\text{O} \equiv 8$  68

3.3 Spectroscopical characteristics of the compound 8 68

3.4 Discussion of the structure 70

3.5 Deprotonation and sphere - cation interaction 73

3.6 Visualizing the  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  type clusters' aggregation with scanning  
electron microscope (SEM) 74

3.7 Discussions and perspectives 77

## Chapter 4

Surface Reactions Inside the Porous Nanocapsule Cavity Tuning the  
Internal Capsule Functionalities 79

4.1 Introduction 79

4.2 Syntheses and the characterization of compounds 9-12 82

4.3 Synthesis and characterization of  
 $(\text{NH}_4)_{42}\{[(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6]_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})\}_{30}\}\cdot\text{ca.}300\text{H}_2\text{O}\cdot\text{ca.}10$   
 $\text{CH}_3\text{COONH}_4 \equiv 1$  (102) 83

4.4 Synthesis and characterization of  
 $(\text{NH}_4)_{42}\{[(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6]_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}=\text{CHCOOH}_{\text{cis}})\}_{30}\}\cdot$   
 $\text{ca.}300\text{H}_2\text{O} \equiv 9$  83

4.5 Synthesis and characterization of  
 $(\text{NH}_4)_{42}\{[(\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6)_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}(\text{OH})\text{CH}_3)_{30}\}\}\cdot\text{ca.}250$   
 $\text{H}_2\text{O} \equiv 10$  84

4.6 Synthesis and characterization of  
 $(\text{NH}_4)_{42}\{[(\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6)_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}_2\text{COOH})_{28}(\text{CH}_3\text{COO})_2\}\}\cdot$   
 $\text{ca.}250\text{H}_2\text{O}\cdot3(-\text{OOCCH}_2\text{COOH}) \equiv 11$  84

4.7 Synthesis and characterization of

$[(\text{CH}_3)_2\text{NH}_2]_{42}[\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}_2\text{CH}_2\text{COOH})\}_{30}]\cdot\text{ca.}300\text{H}_2\text{O} \equiv 12 \ 85$

4.8 Properties of the structures 85

4.9 Ligand-exchange at the internal sites 86

4.10 Disorder problems in the crystal structure determinations induced by the ligands 87

4.11 How the shell functionality of the cavity is tuned from hydrophilic to hydrophobic 88

4.12 Characteristic vibrational spectroscopy for compounds 9 - 12 89

4.13 Nuclear magnetic resonance studies of compounds 9 - 12 90

4.14 Discussions and perspectives 94

## Chapter 5

Synthesis and Characterization of Spherical Giant Polyoxomolybdates as “Substrate Specific Nanosponges” 95

5.1 Introduction 95

5.2 Synthesis and characterization of compounds 13 and 14 97

5.3 Synthesis and characterization of  $\text{Na}_{11}[(\text{CH}_3)_2\text{NH}_2]_{33}[\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})\}_{30}]\cdot\text{ca.}\{300\text{H}_2\text{O} + \text{CH}_3\text{COO}^- + (\text{CH}_3)_2\text{NH}_2^+\} \equiv 13 \ 97$

5.4 Synthesis and characterization of  $[(\text{CH}_3)_2\text{NH}_2]_{42}[\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{H}_2\text{PO}_2)\}_{30}]\cdot\text{ca.}300\text{H}_2\text{O} \equiv 14 \ 98$

5.5 Structural details of the cluster anions 13a and 14a 98

5.6 Crown-ether type behaviour on the pore sites of the giant spherical polyoxometalates 101

5.7 Synthesis and characterization of uranium-containing cluster compound 17

$(\text{NH}_4)_{60}\{\text{U}_3\text{C}\{\text{Mo}^{\text{VI}}\text{Mo}_5^{\text{VI}}\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}_2^{\text{V}}\text{O}_4(\text{SO}_4)\}_{30}\}\cdot 308\text{H}_2\text{O} \equiv 17 \ 103$

5.8 Characteristic vibrational and electronic absorption spectroscopy for compounds 13, 14 and 17 103

5.9 Electronic spectra of compound 17 106

5.10 Magnetic susceptibility measurements on 17 107

5.11 EPR spectrum of 17 108

5.12 Discussions and perspectives 109

## Chapter 6

Observation on Dynamic Equilibria Between Inside and Outside Guests of the  $\{Mo_{132}\}$  Type Capsule 111

6.1 Introduction 111

6.2 Studies on the  $\{Mo_{132}\}$  type polyoxometalate capsule's internal equilibria 112

6.3 Synthetical approaches for tuning the charge of the  $\{Mo_{132}\}$  type capsule as function of pH 113

6.4 Stability investigation and charge tuning of  $\{Mo_{132}\}$  type spherical polyoxomolybdate cluster anions studied using Raman spectroscopy 115

6.5 Ligand exchange investigation using  $^1H$  NMR in the  $\{Mo_{132}\}$  type cluster in function of time 118

6.6 pH dependent  $^1H$  NMR equilibria studies on the  $\{Mo_{132}\}$  type capsule 121

6.7 Temperature dependent  $^1H$  NMR equilibria studies on the  $\{Mo_{132}\}$  type capsule 123

6.8 Influence of the proton concentration on the exchange studied by titration 125

6.9 Summary and conclusion 126

## Chapter 7

Supramolecular Chemistry on Cluster Surface; Tentative Complexation of Lithium and Ammonium Cations on  $\{Mo_{57}\}$  Type Cluster 127

7.1 Introduction 127

7.2 Synthesis and characterization of compound 15 128

7.3 Discussion of the problem 129

7.4 Conclusions and perspectives 131

## Chapter 8

Summary and conclusion 133

## Chapter 9

Appendix I: Experimental methods 137

9.1. Elemental analyses 137

9.2 Vibrational spectroscopy 137

9.3 Electronic absorption spectroscopy 137

9.4 MALDI TOF MS 137

9.5 Bond Valence Sum calculations 138

9.6 Thermogravimetric measurements 138

9.7 Nuclear magnetic resonance 138

9.8  $^{57}\text{Fe}$  Mössbauer spectroscopy 139

9.9 Potentiometric titration 139

9.10 Magnetic studies 139

Appendix II : TG - DTA spectra of compounds listed in the thesis 140

## Chapter 10

Crystal data for compounds listed in the thesis 149

10.1 Single crystal X-ray structure analysis 149

Bibliography 155

## Keywords

polyoxometalates • electron delocalization • host-guest chemistry • Keplerate • Keggin polyoxomolybdates • proton-coupled electron transfer • nanoacids • single crystal X-ray studies • dicarboxylic acids • NMR spectroscopy • equilibrium studies • cation uptake • crown-ether type functions.

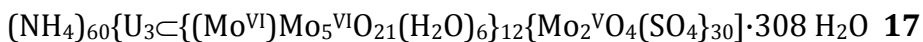
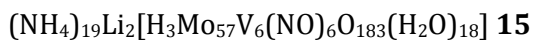
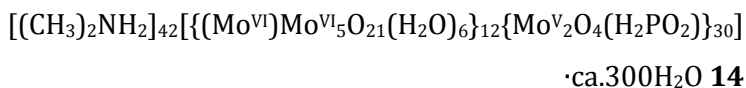
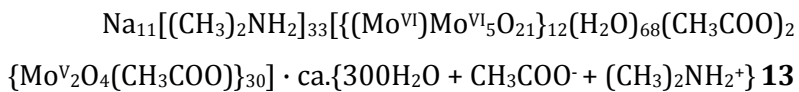


## List of compounds described in this dissertation <sup>1</sup>

- $(\text{NH}_4)_{42}[\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})\}_{30}]$   
·ca.300H<sub>2</sub>O·ca.10CH<sub>3</sub>COONH<sub>4</sub> **1\***
- $[\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}\text{O}_{252}(\text{CH}_3\text{COO})_{12}\{\text{Mo}_2\text{O}_7(\text{H}_2\text{O})\}_2\{\text{H}_2\text{Mo}_2\text{O}_8(\text{H}_2\text{O})\}(\text{H}_2\text{O})_{91}]$   
·ca.150H<sub>2</sub>O **2\***
- $[(\text{NH}_4)_{72}\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{SO}_4)\}_{30}]$ ·ca.200H<sub>2</sub>O **3\***
- $[\text{H}_x\text{PMo}_{12}\text{O}_{40}\text{cH}_4\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}(\text{CH}_3\text{COO})_{15}\text{O}_{254}(\text{H}_2\text{O})_{98}]$ ·ca.60H<sub>2</sub>O **4\***
- $\text{Na}_4[\text{SiMo}_{12}\text{O}_{40}\text{cH}_4\text{Mo}^{\text{VI}}_{70}\text{Mo}^{\text{V}}_2\text{Fe}^{\text{III}}_{30}\text{O}_{254}(\text{H}_2\text{O})_{98}(\text{CH}_3\text{COO})_{16}]$   
·ca.60H<sub>2</sub>O **5**
- $[\text{AsMo}_{12}\text{O}_{40}\text{cH}_4\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}\text{O}_{252}(\text{H}_2\text{O})_{98}(\text{CH}_3\text{COO})_{15}]$ ·ca. 60H<sub>2</sub>O **6**
- $[\text{HPW}^{\text{VI}}_{11}\text{W}^{\text{VO}}_{40}\text{cMo}^{\text{VI}}_{65}\text{W}^{\text{VI}}_7\text{Fe}^{\text{III}}_{30}(\text{CH}_3\text{COO})_{15}\text{O}_{252}(\text{H}_2\text{O})_{98}]$ ·ca.120H<sub>2</sub>O **7**
- $\text{Ba}_5[\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}\text{O}_{252}(\text{CH}_3\text{COO})_{15}\{\text{Mo}_2\text{O}_7(\text{H}_2\text{O})\}_2\{\text{Mo}_2\text{O}_8(\text{H}_2\text{O})\}$   
 $(\text{OH})_{10}(\text{H}_2\text{O})_{81}]$ ·ca.150H<sub>2</sub>O **8**
- $(\text{NH}_4)_{42}[\{(\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6)\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}=\text{CHCOOH}_{\text{cis}})\}_{30}]$   
·ca.300 H<sub>2</sub>O **9**
- $(\text{NH}_4)_{42}[\{(\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6)\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}(\text{OH})\text{CH}_3)\}_{30}]$   
·ca.250 H<sub>2</sub>O **10**
- $(\text{NH}_4)_{42}[\{(\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6)\}_{12}$   
 $\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}_2\text{COOH})_{28}(\text{CH}_3\text{COO})_2\}]$ ·ca.300 H<sub>2</sub>O **11**
- $[(\text{CH}_3)_2\text{NH}_2]_{42}[\{(\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6)\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{OOCCH}_2\text{CH}_2\text{COOH})\}_{30}]$   
·ca.300H<sub>2</sub>O **12**

---

<sup>1</sup> The compounds which have been synthesized by the author as the result of the research work and also those which have not been synthesized by the author, marked with (\*), but have been referred to in the following chapters for easy reference.



## Introduction

The work done as part of this thesis was principally oriented towards the synthesis and characterization of nanometer-scale inorganic molecules and clusters belonging to the family of polyoxomolybdates.

The investigation carried out in course of this thesis revealed potential host functionalities of the spherical shaped polyoxomolybdates, especially the host-guest chemistry of the  $[\text{Mo}_{72}\text{Fe}_{30}]$  spherical type clusters, the aim was to understand the dynamics of the host-guest interaction processes in aqueous solution.

Another point of interest referred to the nanosized cluster species that can be constructed as derivatives of the spherical, soluble capsules of the type  $(\text{pentagon})_{12}(\text{linker})_{30}$ . The robust spherical skeleton exhibits 20 pores and 20 channels ending in the nanosized cavity. The challenge was to modify and to tune these anionic capsules to present different kind of interior surfaces, pores with different sizes and properties, different overall charges. The aim was to study these interactions, how they take place in function of the acidity, temperature and time.

Interestingly these capsules can be described as artificial cells and allow a new related chemistry, e. g. modelling of passive ion transport through the related inorganic membrane as well as cell response to stimulation.

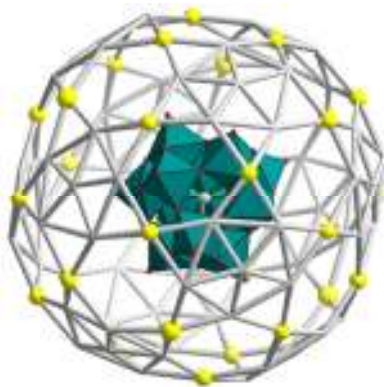
The present dissertation is divided on two parts, first the theoretical part, which is described in Chapter 1 and the experimental part, which includes the chapters 2 – 7 containing the original results obtained through the research period. Every chapter starts with an introductory short theoretical description.

## Synopsis of the main parts of the thesis

The first chapter of this work, called “**Theoretical background of the polyoxomolybdate chemistry**” presents a short history of polyoxometalates based on metal-oxides starting with Berzelius, who in 1826 described the yellow precipitate that is produced when ammonium molybdate is added to phosphoric acid and which is now known as ammonium-12-molybdophosphate,  $(\text{NH}_4)_2\text{PMo}_{12}\text{O}_{40}$  aq., going through the first attempts to understand the composition of the heteropolyanions, stopping by the modern Isopolyoxometalates with giant spherical structures prepared by the group of A. Müller. The introductory chapter continues with a few topics about the formation of the polyoxometalates and some examples of the spherical and wheel type structures.

The second chapter called “**A Unique Metal-Oxide Based Reduced Hybrid: Core-Shell Electron Transfer upon Encapsulation**” contains the synthesis and the detailed analyses of a supramolecular host-guest type polyoxometalate cluster of the type  $[\text{SiMo}_{12}\text{O}_{40}\text{C}\text{Mo}^{\text{VI}}_{70}\text{Mo}^{\text{V}}_2\text{Fe}^{\text{III}}_{30}]$ . The goal was to find an optimal preparation method in order to obtain the supramolecular entities in high yield and high purity. The encapsulation of the Keggin anion inside the cavity of the host type cluster was proved with infrared, electronic and Raman spectroscopy, Mössbauer,  $^{31}\text{P}$ -NMR and single crystal analysis. We considered the competition between metal-oxide based core-shell components with electron acceptor properties (the core can be considered as a quantum dot), while additionally competition of the electrons for  $\text{Fe}^{\text{III}}$  and  $\text{Mo}^{\text{VI}}$  centers is present because the  $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$  and  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  couples have nearly

equal redox potentials. Spectroscopic data clearly establish that these host-guests systems contain non-reduced Keggin anions and reduced shells. The results can be explained in a simple view: Electrons “prefer” to escape as usual to the periphery of a system and the delocalization in larger areas (here of (Mo)Mo<sub>5</sub> type), while the extent of delocalization via Fe(III) linkers over the shell remains to be determined. Further studies are planned to get a deeper insight the formation mechanism of these fascinating systems, and in particular to specify the role of (possibly proton-coupled) electron transfers.



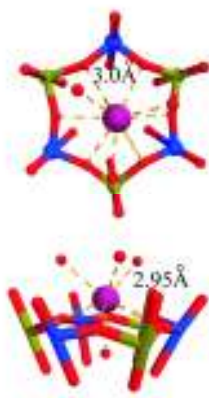
**Figure 1.** Combined polyhedral – wire frame representation of  $[\text{SiMo}_{12}\text{O}_{40}\text{Mo}^{\text{VI}}_{70}\text{Mo}^{\text{V}_2}\text{Fe}^{\text{III}}_{30}]$ : the metal  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  capsule in wire frame representation - with 30  $\text{Fe}^{\text{III}}$  centers (highlighted as yellow spheres) linking the 12  $\{(\text{Mo})\text{Mo}_5\}$  type pentagonal units- and the Keggin nucleus (idealized) in polyhedral representation.

The third chapter of this work, called “**Molybdenum-Oxide Based Unique Nanoacid of the Type  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  Showing Deprotonation and Interaction with Alkali Earth Metal Cations**”, describes a newly synthesized compound which underlines the acidic properties of the  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  type spherical cluster, in which synthetical route happens a deprotonation and a reaction with alkali cations, i.e.

barium. The neutral  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  contains thirty acidic sites, the water molecules are linked covalently to the iron centers. Stepwise addition of the sodium hydroxide to aqueous solution of  $\{\text{Mo}_{72}\text{Fe}_{30}\}$ , taking in consideration the fast change in the pH of the solution, can lead to three types of reactions:

- Deprotonation of the acidic water ligands on the iron sites.
- Condensation of the aquahydroxo- complexes with elimination of water and formation of Fe-O-Fe, Fe-OH-Fe, or in the present case Ba-O-Fe between the initially discrete clusters.
- Decomposition at alkaline pH.

The compound  $\{\text{Ba}_5\text{Mo}_{72}\text{Fe}_{30}\}$  consists of macroions  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  linked by barium atoms, in the synthetical method the pH is carefully chosen, the reason for it is to achieve an adequate charge of the anion clusters (-10) and further reaction of them with barium cations in form of chloride salt in solution.

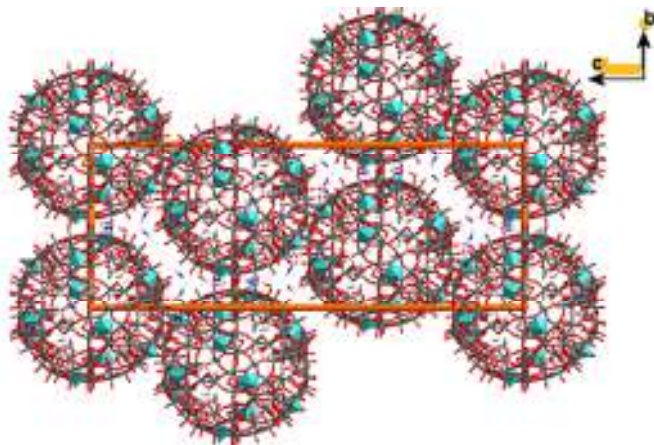


**Figure 2.** Wire-frame representation of one of the  $[\text{Ba}(\text{H}_2\text{O})_9]^{2+}$  complexes interacting through hydrogen bonds with one of the  $\{\text{Mo}_3\text{Fe}_3\text{O}_6\}$  type pores of the capsule  $\{\text{Ba}_5\text{Mo}_{72}\text{Fe}_{30}\}$ ; Color code: Mo – blue, Fe – green, Ba – violet, O – red.

Chapter 4 called **“Surface Reactions Inside the Porous Nanocapsule Cavity Tuning the Internal Capsule Functionalities”** describes four of the novel synthesized compounds which show internal functional properties, where ligand exchange was studied inside the cavity of the  $\{\text{Mo}_{132}\}$  type spherical cluster, the acetate ligands being replaced by organic acid ligands with more than one functional group (e. g. organic acids with a strong acid character like maleic-, malonic-, lactic- and succinic acid). The ligand exchange takes place at room temperature and low pH induced by dissolution of the dicarboxylic acids in water. The modification of the cluster interior can be carried out by tuning the nature of the ligands associated with the  $\{\text{Mo}^{\text{V}}_2\}$  linkers. The use of dicarboxylate ligands with “free” non-coordinating deprotonated acidic groups in the  $\{\text{Mo}_{132}\}$  type capsules opens perspectives for studying structuring processes in which electrolyte hybrids are generated while this procedure may be extended to encapsulated magnetic metal ion aggregates, too. The generation of the deprotonated form is especially important because of their high directing power. Based on the present results, it becomes also feasible to study the selectivity of encapsulated ions for specific recognitions based on dicarboxylic acids on a molecular scale, for instance with calcium ions, where the interactions are known to be quite strong.

Chapter 5 called **“Synthesis and Characterization of Spherical Giant Polyoxomolybdates as Substrate Specific Nanosponges”** focuses on the single crystal’s structures, unit cell dimensions and easy understanding of the linkage of atoms, group of atoms, building units, building blocks on molecular level. The question comes up regarding the

crystal's structure, the possibility to synthesize similar compounds to  $\{\text{Mo}_{132}(\text{acetate})_{30}\}$  with lower symmetry, leading to a better understanding of the molecular structure, an easier refinement of the structure and recognition of the disorder inside these molecules with more than 500 atoms. The “one-pot” syntheses are planned under well defined parameters, but the packing of the atoms is hard to be controlled. Finally it is reached the new compound with the  $\{\text{Mo}_{132}\}$  type skeleton, having thirty acetate ligands inside the cavity and as countercations in the lattice are the dimethyl-ammonium cations, packed in a rhombohedral crystal system, space group R-3.



**Figure 3.** Representation of packing of  $\{\text{Na}_{11}[(\text{CH}_3)_2\text{NH}_2]_{33}\text{Mo}_{132}\}$  in the crystal lattice (ball-and-stick/polyhedral model viewed along the  $b$  and  $c$  parameter directions). The spherical anions, the outer surface of which is formed by terminal oxygen atoms, are organized in a rhombohedral packing.

This chapter is dedicated also to the description of unusual spherical molybdenum-oxide based nanoobjects, capable of responsive reactivity - like that of a nanosponge bearing sizeable  $\{\text{Mo}_n\text{O}_m\}$  ring like pores - which may allow new techniques in supramolecular



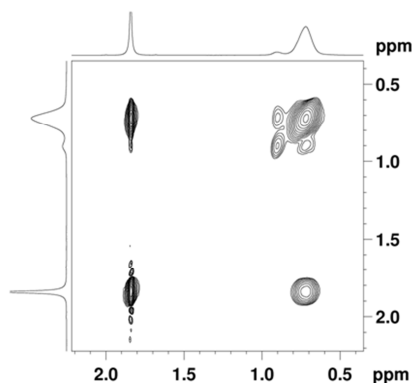
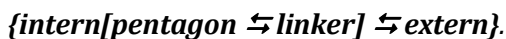
nanotechnology regarding efficient and specific recognition by a large number of pores/receptor sites, which are similar to those of macrocyclic ligands. The maximum pore diameter of a related  $\{\text{Mo}_n\text{O}_m\}$  ring is now ca. 0.8 nm. The pores are sizeable since fixed basic pentagonal  $[(\text{Mo})\text{Mo}_5]$  type units of the object  $[(\text{pent})_{12}(\text{linker})_{30}]$  can be connected with different linkers.

The present results can be considered as a starting point for a sphere surface- and nanoporous cluster-chemistry with significant interdisciplinary aspects for modelling spherical virus surfaces, (106) as well as catalytic and biomimetic processes because of the simultaneous presence of large pores providing access to the nano-sized cavities. It might be mentioned here, that spherical object tiling is important for understanding virus structure, for the construction of Buckminster Fuller domes.

The sixth chapter called **“Observation on Dynamic Equilibria Between Inside and Outside Guests of the  $\{\text{Mo}_{132}\}$  Type Capsule”** describes stability investigations and dynamic equilibria studies, performed through nuclear magnetic resonance measurements and additionally the Raman spectroscopical method was used for charge-tuning investigations in the  $\{\text{Mo}_{132}\}$  type cluster. The attractiveness of research of capsular complexes is discussed regarding the challenge of understanding the mechanisms of guest entry and exit. This is considered as practically a new subject and refers to open container molecules considering also the extremes of no measurable guest exchanges. It is possible to study the type of exchange for polytopic hosts with unprecedented dynamical equilibria for the guests on multiple

coordination sites inside the capsule. Under formal consideration this is a situation of a cell interacting specifically with its environment regarding a substrate and showing related inside dynamics, too.

Most important, there is without any doubt according to the EXSY spectrum (Figure 4) not only an exchange between internal and external acetates in the  $\{Mo_{132}\text{-acetate}\}$  (peaks at 0.7, 1.85 ppm), but also between the internal sites (peaks at 0.7, 0.9). However, the acetates associated with the pentagons do not show an appreciable exchange with the external ones. The overall exchange situation may be represented by



**Figure 4.** Room temperature  $^1H$  EXSY spectrum of the solution of  $\{Mo_{132}\text{-acetate}\}$  in  $D_2O$  (pH = 5.10) (mixing time of 1 s).

The inside and outside substrates'/ligands, i.e. acetate exchange, and the unprecedented observation of dynamical internal equilibria, can be observed due to compartmentalization, i.e. separation of the “inside” from the “outside” by the porous nanocapsule. The communication of the substrates is controlled by their coordination strength to the capsule, the

capsule pore flexibility and signals from the outside, such as variations in the H<sup>+</sup> concentration. Based on these results there is the option to perform related studies based on different substrates

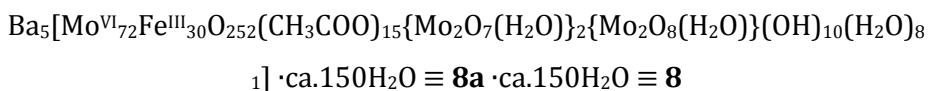
Chapter 7 entitled “**Supramolecular Chemistry on Cluster Surface; Tentative Complexation of Lithium and Ammonium Cations on {Mo<sub>57</sub>} Type Cluster**”, called tentative because we intended to complexate more lithium cations than two in the cluster compound. The present result, which was already anticipated by theoretical chemists, could initiate new investigations regarding the study of counterion distribution on surfaces of large metal-oxide based clusters having specific surface functionalities such that selective nanoscale complexation of cations is possible.

In the chapter 8 “**Summary and conclusions**” are presented the conclusions and results of the research.

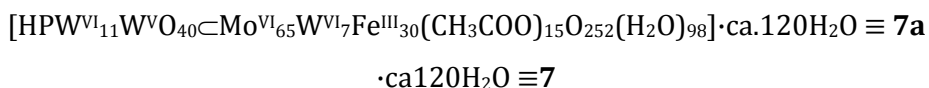
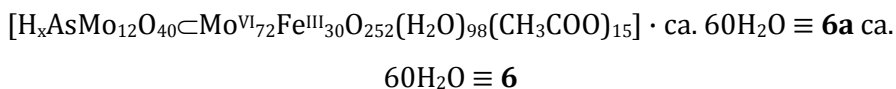
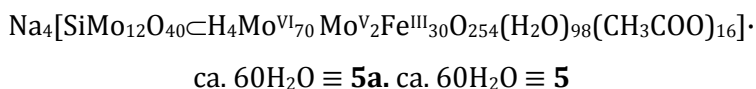
Large complex molecules of the nanocosmos - like proteins - can do things like activating, storing, transferring complex information, transporting and separating substrates and related functions with a high precision. The unusual and absolutely unique chemistry of oxomolybdates - under reducing conditions offers the option to generate related nanosystems. In the solution of oxoanions of the early transition metals (like molybdenum) - controlled linking of metal-oxide building blocks from a 'virtual library' - provides the option to get exquisite molecular architecture. Such architecture constitutes two broad classes: the molybdenum 'blues' and 'browns'. In this dissertation some clusters of “molybdenum browns” classes have been isolated, characterized and studied in detail.

Synthetic investigation of the known systems opened up new ways, which were systematically studied, transcending the known regime of covalent chemistry crystallized at the 'supramolecular frontier'. New effects were observed; those understood were exploited and have been described here. Unanswered questions remain.

Regarding host-guest chemistry of polyoxometalates involving the  $\{\text{Mo}_{72}\text{Fe}_{30}\}$  type cluster, there was shown an interesting property of the cluster, being as the largest inorganic acid till present, able for deprotonation at the Fe-OH<sub>2</sub> sites and its interaction with alkali earth metals:

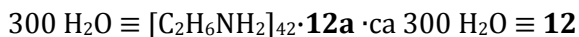
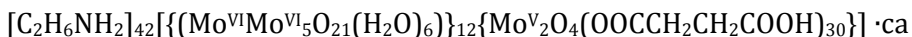
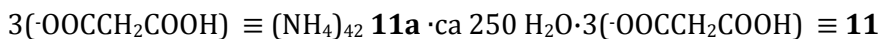
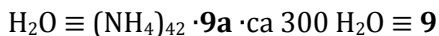
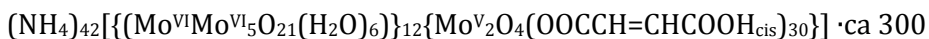


Remaining at the same idea of the host-guest formation ability, it was also observed that there exist other sites beneath the cluster surface, where smaller inorganic Keggin type anions, like  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ ,  $[\text{AsMo}_{12}\text{O}_{40}]^{3-}$ ,  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  could be placed. The formation of **5a**, **6a** and **7a** from **2a** (generated in "one-pot" synthesis) proved such expectation:

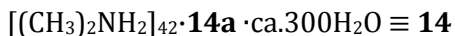
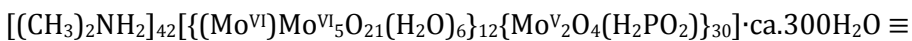
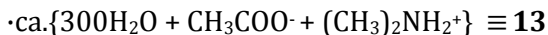
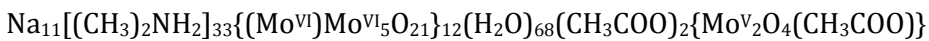


In the matter of inner ligand exchange chemistry involving the  $\{\text{Mo}_{132}\}$  type cluster, it was observed that there exist possibilities to fine-tune the inner surface of a cluster cavity, covalently attached to the

linkers, where dicarboxylic acids could replace acetate with maleic-, malonic-, lactic- and succinic acids. The formation of **9a**, **10a** and **11a** and **12a** proved such expectation:



Within the context of host-guest chemistry the presence of related  $\{\text{Mo}_9\text{O}_9\}$  crown-ether type rings in the  $\{\text{Mo}_{132}\}$  type spherical clusters did not escape attention. This dissertation demonstrated that cluster, like **1a** with appropriate  $\{\text{Mo}_9\text{O}_9\}$  pore size could for instance bind, large organic cations like dimethyl-ammonium present in the solution leading to the formation of **13a** and **14a**. Because of such substrate specific behaviour, they can be called dimethyl-ammonium “nanosponges”:



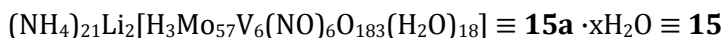
The phenomena within the context of host-guest chemistry related to 'uptake' of cationic species described so far have been observed

by the precipitation of crystals of the corresponding complexes. But there is a question about the equilibrium of these systems. Chapter 6 gives some answers on the dynamic equilibria between the inside and outside guests of the cluster molecule. There was studied the stability of the  $\{\text{Mo}_{132}\}$  type cluster with synthetic methods, NMR studies and Raman measurements.

Is it possible to study those processes at least qualitatively, now it is given the answer based on the NMR studies, quantitatively, too. The stability studies were performed principally by Raman spectroscopy in water and it was observed that the clusters investigated retain their molybdenum-oxide skeleton when dissolved in water and remain stable on room temperature and can be concluded that after titration with sulphuric acid and hydrochloric acid, the integrity of **1** =  $\{\text{Mo}_{132}(\text{CH}_3\text{COO})_{30}\}$  cluster remains till pH 2.

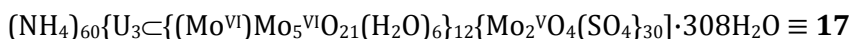
The inside and outside substrates'/ligands, i.e. acetate exchange, and the unprecedented observation of dynamical internal equilibria, can be observed due to compartmentalization, i.e. separation of the "inside" from the "outside" by the porous nanocapsule. The communication of the substrates is controlled by their coordination strength to the capsule, the capsule pore flexibility and signals from the outside, such as variations in the  $\text{H}^+$  concentration. Based on these results there is the option to perform related studies based on different substrates.

In the idea of the surface functionalities of the polyoxomolybdate cluster, it was planned the new  $\{\text{Mo}_{57}\}$  type cluster:



which exhibits a growth process in six external holes and could be investigated its interaction with cations for mimicking specific properties of transition metal oxide surfaces. A future challenging aspect would be to distinguish between specific cation coordination and non-specific ion-pairing - which is the actual case - as both facilitate the formation of giant assemblies of metal-oxide based macroions owing to a decrease of repulsion.

In the  $\{\text{Mo}_{132}\}$  type giant cluster the flexible ring shaped  $\{\text{Mo}_9\text{O}_9\}$  type pores permit also entry of smaller cationic guests, which finally will get linked to the ligands attached to the dinuclear  $\{\text{Mo}_2\}$  units. Such cations are known from literature, sodium, potassium, cerium, and now it was synthesized the uranium containing  $\{\text{Mo}_{132}\}$  type capsule, where the uraniums are bound to the sulphate ligand of the cluster sphere:



The dissertation continues with a chapter 9 called “**Appendix I Experimental methods and Appendix II TG-DTA spectra of compound listed in the thesis**” that describes the methods used on compounds to determine the properties and structure characteristics.

The chapter 10 includes tables with “**Crystal data for the compounds listed in the thesis**”, this is followed by the “**Bibliography**” at the end.

## Bibliography

1. A. Hatzor-de Picciotto, A. D. Wissner-Gross, G. Lavalley, P. S. Weiss, *Journal of Experimental Nanoscience*, **2007**, *2*, 3-11.
2. J. M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, Weinheim : VCH, **1995**.
3. J. M. Lehn, *Pure Appl. Chem*, **1978**, *50*, 871-892.
4. J. M. Lehn, *Angew. Chem. Int. Ed.*, **1990**, *29*, 1304-1319.
5. Baxter, P. N. W. [book auth.] J. E. D. Davies, D. D. MacNicol, F. Vogtl and J. M. Lehn J. L. Atwood. *Comprehensive Supramolecular Chemistry*. Vol 9. Oxford : Pergamon/Elsevier, **1996**.
6. G. V. Oshovsky, D. N. Reinhoudt, W. Verboom, *Angewandte Chemie Int. Ed.*, **2007**, *46*, 2366-2393.
7. J. Emsley, *Nature's building blocks*. Oxford : Oxford University Press, **2001**, pp. 262-266.
8. J. Berzelius, *Pogg. Ann.*, **1826**, *6*, 380.
9. H. Struve, L. Svanberg, *J. Prakt. Chem.*, **1848**, *44*, 291.
10. C. Marignac, *C. R. Acad. Sci.*, **1862**, *55*, 888.
11. R. Pizzighelli, A. Miolati, *J. Prakt. Chem.*, **1908**, *77*, 417.
12. M. T. Pope, *Heteropoly and isopoly oxometalates*. Berlin : Springer, **1983**.
13. L. C. Pauling, *J. Am. Chem. Soc.*, **1929**, *51*, 2868.
14. J. F. Keggin, *Nature*, **1933**, *131*, 908.
15. J.W. Illingworth, A.J. Bradley, *Proc. Roy. Soc. A*, **1936**, *157*, 113.
16. H. T. Evans, Jr., *J. Am. Chem. Soc.*, **1948**, *70*, 1291.
17. H. T. Evans, Jr., *J. Am. Chem. Soc.*, **1968**, *90*, 3275.
18. M.T. Pope, H. So, *Inorg. Chem.*, **1972**, *11*, 1441-1443.
19. J. Aveston, *Inorg. Chem.*, **1964**, *31*, 981-986.
20. W. Shum, W.G. Klemperer, *J. Am. Chem. Soc.*, **1976**, *98*, 8291-8293.
21. L. Pettersson, *Molecular Engineering*, **1993**, *3*, 29-42.
22. L. Cronin, E. Diemann, A. Müller. [ed.] J. Derek Woollins. *Inorganic Experiments*. 2nd Ed., Wiley-VCH, **1993**, pp. 340-346.
23. [http://en.wikipedia.org/wiki/X-ray\\_crystallography](http://en.wikipedia.org/wiki/X-ray_crystallography). [Online]
24. T. Liu, B. Imber, E. Diemann, G. Liu, K. Cokleski, H. Li, Z. Chen, A. Müller, *J. Am. Chem. Soc.*, **2006**, *128*, 15914-15920.
25. L. Liu, T. Liu, *Langmuir*, **2005**, *21*, 2713-2720.
26. D. L. Kepert, *Inorganic Chemistry*, **1969**, *8*, 1556-1558.
27. H.T. Evans, Jr., *Perspec. Struct. Chem.*, **1971**, *4*, 1.
28. A. Müller, S. Roy, *Coordination Chemistry Reviews*, **2003**, *245*, 153-166.



29. A. Müller, P. Kögerler, H. Bögge, *Structure & Bonding*, **2000**, 96, 203-236.
30. D. G. Kurth, P. Lehmann, D. Volkmer, H. Cölfen, M. J. Koop, A. Müller, A. Du Chesne, *Chemistry - A European Journal*, **2000**, 6, 385-393.
31. D. G. Kurth, D. Volkmer, M. Ruttorf, B. Richter, A. Müller, *Chemistry of Materials*, **2000**, 12, 2829-2831.
32. D. G. Kurth, P. Lehmann, D. Volkmer, A. Müller, D. Schwahn, *Dalton Transactions*, **2000**, 3989-3998.
33. D. Volkmer, A. Du Chesne, D. G. Kurth, H. Schnablegger, P. Lehmann, M. J. Koop, A. Müller, *J. Am. Chem. Soc.*, **2000**, 122, 1995-1998.
34. D. Gatteschi, L. Pardi, A. L. Barra, J. Döring. *Nature*, **1991**, 354, 463-465.
35. A. Müller, E. Diemann, C. Kuhlmann, W. Eimer, C. Serain, T. Tak, A. Knöchel, P. K. Pranzas, *Chem. Commun.*, **2001**, 1928-1929.
36. Liu, T, *J. Am. Chem. Soc.*, **2002**, 124, 10942-10943.
37. T. Liu, E. Diemann, H. Li, A. W. M. Dress, A. Müller, *Nature*, **2003**, 426, 59-62.
38. A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.*, **1998**, 98, 239-271.
39. A. Müller, M. T. Pope, *Angew. Chem. Int. Ed.*, **1991**, 30, 34-38.
40. D. Voet, J. G. Voet. *Biochemistry*. 2nd. Ed., New York : Wiley, **1995**, p. 1076.
41. A. Müller, J. Meyer, E. Krickemeyer, C. Beugholt, H. Bögge, F. Petres, M. Schmidtman, P. Kögerler, M. J. Koop, *Chemistry - A European Journal*, **1998**, 4, 1000-1006.
42. A. Müller, E. Beckmann, H. Bögge, M. Schmidtman, A. Dress, *Angew. Chem. Int. Ed.*, **2002**, 41, 1162-1167.
43. A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtman, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem. Int. Ed.*, **1999**, 38, 3238-3241.
44. A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtman, P. Kögerler, B. Hauptfleisch, S. Leiding, K. Wittler, *Angew. Chem. Int. Ed.*, **2000**, 39, 1614-1616.
45. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, F. Peters, *Angew. Chem. Int. Ed.*, **1998**, 37, 3360-3363.
46. A. Müller, S. K. Das, P. Kögerler, H. Bögge, M. Schmidtman, A. X. Trautwein, V. Schünemann, E. Krickemeyer, W. Preetz., *Angew. Chem. Int. Ed.*, **2000**, 39, 3414-3417.

47. A. Müller, S. K. Das, H. Bögge, M. Schmidtman, A. Botar, A. Patrut, *Chem. Commun.*, **2001**, 657-658.
48. J. M. Lehn, *Chem. Soc. Rev.*, **2007**, 36, 151-160.
49. M. Kemp, *Kepler's cosmos, Nature*, **1998**, 393, 123.
50. A. Müller, M. T. Pope. *Polyoxometalate Chemistry*. Netherlands : Kluwer Academic Publishers, **2001**, pp. 301-318.
51. A. Müller, M. Koop, H. Bögge, M. Schmidtman, C. Beugholt, *Chem. Commun.*, **1998**, 1501-1502.
52. A. Müller, C. Beugholt, M. Koop, S. K. Das, M. Schmidtman, H. Bögge, *Z. Anorg. Allg. Chem.*, **1999**, 625, 1960-1962.
53. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, P. Kögerler, C. Rosu, E. Beckmann, *Angew. Chem. Int. Ed.*, **2001**, 40, 4034-4037.
54. C. Serain, A. Müller, *Acc. Chem. Res.*, **2000**, 33, 2-10.
55. A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem. Int. Ed.*, **1995**, 34, 2122-2124.
56. A. Müller, S. K. Das, V.P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtman, B. Hauptfleisch, *Z. Anorg. Allg. Chem.*, **1999**, 625, 1187-1192.
57. A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtman, *Nature*, **1999**, 397, 48-50.
58. A. Müller, B. Botar, S. K. Das, H. Bögge, M. Schmidtman, A. Merca, *Polyhedron*, **2004**, 23, 2381-2385.
59. A. Müller, S. Roy, *Eur. J. Inorg. Chem.*, **2005**, 3561-3570.
60. A. Müller, S. K. Das, H. Bögge, M. Schmidtman, A. Botar, A. Patrut, *Chem. Commun.*, **2001**, 657-658.
61. J. M. Lehn, *Chem. Soc. Rev.*, **2007**, 36, 151-160.
62. <http://darwin-online.org.uk/darwin.html>. [Online]
63. A. Müller, S.K. Das, P. Kögerler, H. Bögge, M. Schmidtman, A.X. Trautwein, V. Schünemann, E. Krickemeyer, W. Preetz, *Angew. Chem. Int. Ed.*, **2000**, 39, 3414-3417.
64. A. Müller, P. Kögerler, A. W. M. Dress, *Coord. Chem. Rev.*, **2001**, 222, 193-218.
65. A. Müller, *Nature*, **2007**, 447, 1035.
66. A. M. Todea, A. Merca, H. Bögge, T. Glaser, J. M. Pigga, M. L. K. Langston, T. Liu, R. Prozorov, M. Luban, C. Schröder, W. H. Casey, A. Müller, *Angew. Chem. Int. Ed.*, **2010**, 49, 514-519.
67. C. Rocchiccioli-Deltcheff, R. Thouvenot, R. Franck, *Spectrochim. acta*, **1976**, 32A, 587-597.

68. A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem. Int. Ed.*, **1999**, *38*, 3238-3241.
69. A. Müller, S. K. Das, E. Krickemeyer, P. Kögerler, H. Bögge, M. Schmidtmann, *Solid State Sci.*, **2000**, *2*, 747-854.
70. C. Sanchez, J. Livage, J. P. Launay, M. Fournier, Y. Jeannin, *J. Am. Chem. Soc.*, **1982**, *104*, 3194-3202.
71. R. Massart, *Ann. Chim.*, **1968**, *3*, 507-512.
72. R. Massart, *Ann. Chim.*, **1969**, *4*, 285-296.
73. J.-M. Fruchart, P. Souchay, *C. R. Acad. Sc. Paris Serie C*, **1968**, *266*, 1571-1574.
74. J. N. Barrows, M. T. Pope, *Advances in Chemistry Series*, **1990**, *226*, 403-417.
75. V. Artero, A. Proust, *Eur. J. Inorg. Chem.*, **2000**, 2393-2400.
76. B. Botar, A. Ellern, R.l Hermann, P. Kögerler, *Angew. Chem. Int. Ed.*, **2009**, *48*, 9080-9083.
77. P. C. H. Mitchell H. F. Barry, *Chemical Uses of Molybdenum*. Goodenough, J. B. [ed.], Michigan : CLIMAX Molybdenum Co., **1982**. Proc. 4th International Conference on Molybdenum.
78. H. Duclusaud, S. A. Borshch, *Inorg. Chem.*, **1999**, *38*, 3489-3493.
79. S. A. Borshch, H. Ducluseaud, J.-J. M. Millet, *Appl. Catal. A General*, **2000**, *200*, 103-108.
80. A. Müller, A. M. Todea, H. Bögge, J. van Slageren, M. Dressel, A. Stammler, M. Rusu, *Chem. Commun.*, **2006**, 3066-3068.
81. A. Müller, E. Krickemeyer, S. K. Das, P. Kögerler, S. Sarkar, H. Bögge, M. Schmidtmann, Sh. Sarkar, *Angew. Chem. Int. Ed.*, **2000**, *39*, 1612-1614.
82. L. An, J. M. Owens, L. E. McNeil, J. Liu, *J. Am. Chem. Soc.*, **2002**, *124*, 13688-13689.
83. A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem. Int. Ed.*, **1999**, *38*, 3238-3241.
84. T. Liu, B. Imber, E. Diemann, G. Liu, K. Cokleski, H. Li, Z. Chen, A. Müller, *J. Am. Chem. Soc.*, **2006**, *128*, 15914-15920.
85. M. L. Kistler, T. Liu, P. Gouzerh, A. M. Todea, A. Müller, *Dalton Trans.*, **2009**, 5094-5100.
86. T. Liu, E. Diemann, H. Li, A. W. M. Dress, A. Müller, *Nature*, **2003**, *426*, 59-62.
87. A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.*, **1999**, 1347-1358.

88. Cronin, L. *Comprehensive Coordination Chemistry II*. Vol. 7 [ed.] T. J. Meyer J. A. McCleverty. Amsterdam : Elsevier, **2004**, pp. 1-56.
89. D.-L. Long, L. Cronin, *Chem. Eur. J.*, **2006**, *12*, 3698-3706.
90. G. Liu, T. Liu, *Langmuir*, **2005**, *21*, 2713-2720.
91. T. Liu, *J. Am. Chem. Soc.*, **2003**, *125*, 312-313.
92. G. Liu, Y. Cai, T. Liu, *J. Am. Chem. Soc.*, 2004, Vol. 126, pp. 16690-16691.
93. G. Liu, T. Liu, *J. Am. Chem. Soc.*, **2005**, *127*, 6942-6943.
94. G. Liu, T. Liu, S. S. Mal, U. Kortz, *J. Am. Chem. Soc.*, **2006**, *128*, 10103-10110.
95. E. J. King, International Encyclopedia of Physical Chemistry and Chemical Physics, Topic 15., Vol. 4, [ed.] J. E. Meyer and F. C. Tompkins E. A. Guggenheim, Oxford : Pergamon Press, **1965**, pp. 218-247.
96. S. F. Lincoln, D. T. Richens and A. G. Sykes. *Comprehensive Coordination Chemistry II*. Vol. 1 [ed.] J. A. McCleverty and T. J. Meyer, Amsterdam : Elsevier, **2004**, pp. 515-555.
97. A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtman, P. Kögerler, B. Hauptfleisch, S. Leiding, K. Wittler, *Angew. Chem. Int. Ed.*, **2000**, *39*, 1614-1616.
98. A. Müller, L. Toma, H. Bögge, M. Henry, E. T. K. Haupt, A. Mix, F. L. Sousa, *Chem. Commun.*, **2006**, 3396-3398.
99. A. Müller, V. P. Fedin, C. Kuhlmann, H. Bögge, M. Schmidtman, *Chem. Commun.*, **1999**, 927-928.
100. A. Müller, Y. Zhou, H. Bögge, M. Schmidtman, T. Mitra, E. T. K. Haupt, A. Berkle, *Angew. Chem.*, **2006**, *118*, 474-479.
101. A. Müller, S. K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bögge, M. Schmidtman, A. Merca, A. Berkle, L. Allouche, Y. Zhou, L. Zhang, *Angew. Chem.*, **2003**, *115*, 5193-5198.
102. A. Müller, S. K. Das, E. Krickemeyer, C. Kuhlmann, *Inorg. Synth.*, **2004**, 191-200.
103. A. Müller, S. Polarz, S. K. Das, E. Krickemeyer, H. Bögge, M. Schmidtman, B. Hauptfleisch, *Angew. Chem. Int. Ed.*, **1999**, *38*, 3241-3245.
104. A. Ziv, A. Grego, S. Kopilevich, L. Zeiri, P. Miro, C. Bo, A. Müller, I. A. Weinstock, *J. Am. Chem. Soc.*, **2009**, *131*, 6380-6382.
105. J. W. Atwood, J. L. Steed, *Supramolecular Chemistry*. Chichester : Wiley, **1991**.
106. D. Voet, J. G. Voet, *Biochemistry*. 2nd. Ed., New York : Wiley, **1995**.
107. A. Müller, S. Roy, *Coord. Chem. Rev.*, **2003**, *245*, 153-166.

108. A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtman, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem. Int. Ed.*, **1999**, *38*, 3238-3241.
109. A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtman, P. Kögerler, B. Hauptfleisch, S. Leiding, K. Wittler, *Angew. Chem. Int. Ed.*, **2000**, *39*, 1614-1616.
110. A. Müller, B. Botar, H. Bögge, P. Kögerler, A. Berkle, *Chem. Commun.*, **2002**, 2944-2945.
111. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, F. Peters, *Angew. Chem. Int. Ed.*, **1998**, *37*, 3363.
112. A. Müller, M. Koop, H. Bögge, M. Schmidtman, C. Beugholt, *Chem. Commun.*, **1998**, 1501-1502.
113. J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*. 2nd. Ed., Chichester : Wiley, **2008**.
114. D.-L. Long, L. Cronin, *Chem. Eur. J.*, **2006**, *12*, 3698-3706.
115. N. Hall, *Chem. Commun.*, **2003**, 803-806.
116. L. Cronin, *Angew. Chem. Int. Ed.*, **2006**, *45*, 3576-3578.
117. P. Gouzerh, M. Che, *L'Actualité Chimique*, **2006**, *298*, 9-22.
118. A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.*, **1999**, 1347-1358.
119. L. Cronin, E. Diemann, A. Müller, *Inorganic Experiments* [ed.] J. D. Woollins. 2nd. Ed., Weinheim : Wiley-VCH, **2003**, pp. 340-346.
120. A. Müller, S. Roy. *The Chemistry of Nanomaterials: Synthesis, Properties and Applications*. [ed.] A. Müller, A. K. Cheetham C. N. R. Rao, Weinheim : Wiley-VCH, **2004**, pp. 452-475.
121. A. Müller, S. K. Das, E. Krickemeyer, C. Kuhlmann, [ed.] J. R. Shapley, *Inorganic Synthesis*, **2004**, *34*, 191-200.
122. A. Müller, D. Rehder, E. T. K. Haupt, A. Merca, H. Bögge, M. Schmidtman, G. Heinze-Brückner, *Angew. Chem. Int. Ed.*, **2004**, *43*, 4466-4470.
123. E. T. K. Haupt, C. Wontorra, D. Rehder, A. Müller, *Chem. Commun.*, **2005**, 3912-3914.
124. D. Rehder, E. T. K. Haupt, H. Bögge, A. Müller, *Chem. Asian J.*, **2006**, *1-2*, 76-81.
125. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, S. Roy, A. Berkle, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3604-3609.
126. B. Alberts, A. Johnson, J. Lewis, M. Raff, K. Roberts, P. Walter. *Molecular Biology of the Cell*. 2nd. Ed., New York : Garland Science, 2002.

127. S. Frings, J. Bradley, [ed.]. *Transduction Channels in Sensory Cells*. Weinheim : Wiley-VCH, **2004**.
128. *Potassium Channels and the Atomic Basis of Selective Ion Conduction (Nobel Lecture)*. R. MacKinnon, *Angew. Chem. Int. Ed.*, **2004**, *43*, 4265.
129. P. Strazzullo, A. Siani, F. P. Cappuccio, M. Trevisan, E. Ragone, L. Russo, F. Stinga, E. Farinano, *Hypertension*, **1998**, *31*, 1284.
130. D. L. Nelson, M. M. Cox, *Lehninger Principles of Biochemistry*. New York : Freemann, **2005**, p. 415.
131. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, B. Botar, M. O. Talismanova., *Angew. Chem. Int. Ed.*, **2003**, *42*, 2085-2090.
132. A. Müller, Y. Zhou, H. Bögge, M. Schmidtman, T. Mitra, E. T. K. Haupt, A. Berkle, *Angew. Chem.*, **2006**, *118*, 474-479.
133. A. Zewail, *Angew. Chem. Int. Ed. Engl.*, **2001**, *40*, 4371-4375.
134. N. N. Greenwood, A. Earnshaw, *Chemistry of Elements*. Oxford : Pergamon, **1989**.
135. A. Ziv, A. Grego, S. Kopilevich, L. Zeiri, P. Miro, C. Bo, A. Müller, I. A. Weinstock, *J. Am. Chem. Soc.*, **2009**, *131*, 6380-6382.
136. E.T.K. Haupt, C. Wontorra, D. Rehder, A. Merca, A. Müller, *Chem. Eur. J.*, **2008**, *14*, 8808-8811.
137. C. Schäffer, H. Bögge, A. Merca, I. A. Weinstock, D. Rehder, E.T.K. Haupt, A. Müller, *Angew. Chem. Int. Ed.*, **2009**, *48*, 8051-8056.
138. D. Gatteschi, R. Sessoli, W. Plass, A. Müller, E. Krickemeyer, J. Meyer, D. Sölter, P. Adler, *Inorg. Chem.*, **1996**, *35*, 1926-1934.
139. A. Müller, W. Plass, E. Krickemeyer, R. Sessoli, D. Gatteschi, J. Meyer, H. Bögge, M. Kröckel, A. X. Trautwein, *Inorg. Chim. Acta*, **1998**, *271*, 9-12.
140. A. Müller, E. Krickemeyer, S. Dillinger, H. Bögge, W. Plass, A. Proust, C. Dloczik, C. Menke, J. Meyer, R. Rohlfing, *Z. Anorg. Allg. Chem.*, **1994**, *620*, 599-619.
141. A. Müller, F. L. Sousa, A. Merca, H. Bögge, P. Miro, J. A. Fernandez, J. M. Poblet, C. Bo. *Angew. Chem.*, **2009**, *121*, 6048-6051.
142. A. Müller, H. Reuter, S. Dillinger, *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 2328-2361.
143. A. Müller, J. Meyer, E. Krickemeyer, C. Beugholt, H. Bögge, F. Petres, M. Schmidtman, P. Kögerler, M. J. Koop, *Chem. Eur. J.*, **1998**, *4*, 1000-1006.
144. R. Billing, D. Rehorek, H. Hennig, *Top. Curr. Chem.*, **1990**, *158*, 151-199.
145. C. Schmuck, *Coord. Chem. Rev.*, **2006**, *250*, 3053-3067.

146. F. Leroy, P. Miro, J. M. Poblet, C. Bo, J. B. Avalos, *J. Phys.Chem. B*, **2008**, *112*, 8591-8599.
147. C. L. Hill, *J. Mol. Catal. A*, **2007**, *262*, 2-6.
148. M. L. Kistler, A. Bhatt, G. Liu, D. Casa, T. Liu. *J. Am. Chem. Soc.*, **2007**, *129*, 6453-6460.
149. A. Müller, W. Plass, E. Krickemeyer, S. Dillinger, H. Bögge, A. Armatage, A. Proust, C. Beugholt, U. Bergmann, *Angew. Chem. Int. Ed. Engl.*, **1994**, *106*, 897-899.
150. D. Gatteschi, R. Sessoli, W. Plass, A. Müller, E. Krickemeyer, J. Meyer, D. Sölter, P. Adler, *Inorg. Chem.*, **1996**, *35*, 1926-1934.
151. V. E. Henrich, P. A. Cox, *The Surface Science of Metal Oxides*. Cambridge : Cambridge University Press, **1996**.
152. A. Nicoara, A. Patrut, D. Margineanu, A. Müller, *Electrochem. Commun.*, **2003**, *5*, 511-518.
153. O. Nagano, A. Kobayashi, Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **1978**, *51*, 790-793.
154. A. Müller, B. Botar, H. Bögge, P. Kögerler, A. Berkle, *Chem. Commun.*, **2002**, 2944-2945.
155. B. Botar, P. Kögerler, C. L. Hill, *Chem. Commun.*, **2005**, 138-3140.
156. A. Müller, A. M. Todea, J. van Slageren, M. Dressel, H. Bögge, M. Schmidtman, M. Luban, L. Engelhardt, M. Rusu, *Angew. Chem. Int. Ed.*, **2005**, *44*, 3857-3861.
157. M.T. Pope, *Comprehensive Coordination Chemistry II*. Amsterdam : Elsevier, **2004**, pp. 635-678.
158. D.-L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.*, **2007**, *36*, 105-121.
159. A. Proust, R. Thouvenot, P. Gouzerh, *Chem. Commun.*, **2008**, 1837-1852.
160. A. Oleinikova, H. Weingärtner, M. Chaplin, E. Diemann, H. Bögge, A. Müller, *ChemPhysChem*, **2007**, *8*, 646-649.
161. G. Liu, M. Cons. T. Liu, *J. Mol. Liq.*, **2005**, *118*, 27-29.
162. T. Liu, E. Diemann, A. Müller, *J. Chem. Educ.*, **2007**, *84(3)*, 526-532.
163. D. Gatteschi, R. Sessoli, W. Plass, E. Krickemeyer, J. Meyer, D. Sölter, P. Adler, *Inorg. Chem.*, **1996**, *35*, 1926-1934.
164. A. Müller, M. Koop, H. Bögge, M. Schmidtman, C. Beugholt, *Chem. Commun.*, **1998**, 1501-1502.
165. A. Müller, S. Polarz, S. K. Das, E. Krickemeyer, H. Bögge, M. Schmidtman, B. Hauptfleisch, *Angew. Chem. Int. Ed.* , **1999**, *38*, 3241-3245.

166. A. Müller, V. P. Fedin, C. Kuhlmann, H. Bögge, M. Schmidtman, *Chem. Commun.*, **1999**, 927-928.
167. A. Müller, S. K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bögge, M. Schmidtman, A. Merca, A. Berkle, L. Allouche, Y. Zhou, L. Zhang, *Angew. Chem.*, **2003**, *115*, 5193-5198.
168. A. Müller, S. K. Das, E. Krickemeyer, C. Kuhlmann, *Inorganic Synthesis*, **2004**, 191-200.
169. A. Müller, Y. Zhou, H. Bögge, M. Schmidtman, T. Mitra, E. T. K. Haupt, A. Berkle, *Angew. Chem.*, **2006**, *118*, 474-479.
170. A. Müller, L. Toma, H. Bögge, M. Henry, E. T. K. Haupt, A. Mix, F. L. Sousa, *Chem. Commun.*, **2006**, 3396-3398.
171. A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtman, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem. Int. Ed. Engl.*, **1999**, *38*, 3238-3241.
172. A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtman, P. Kögerler, B. Hauptfleisch, S. Leiding and K. Wittler. *Angewandte Chemie Int. Ed.*, **2000**, *39*, 614-1616.
173. G. Liu, T. Liu, *Langmuir*, **2005**, *21*, 2713-2720.
174. T. Liu, B. Imber, E. Diemann, G. Liu, K. Cokleski, H. Li, Z. Chen, A. Müller, *J. Am. Chem. Soc.*, **2006**, *128*, 15914-15920.
175. M. L. Kistler, T. Liu, P. Gouzerh, A. M. Todea and A. Müller, *Dalton Trans.*, **2009**, 5094-5100.
176. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, F. Peters, *Angew. Chem. Int. Ed.*, **1998**, *37*, 3360-3363.
177. O. Petina, J. Szakács, D. Rehder, E. T. K. Haupt, A. Müller. **2010**. – in preparation
178. A. M. Todea, J. Szakács, S. Konar, H. Bögge, D. C. Crans, T. Glaser, H. Rousseliere, R. Thouvenot, P. Gouzerh, A. Müller. **2010**. – submitted to *Chem. Eur. J.*
179. J. Szakács, D. Rusu, M. Rusu, **2010** – submitted to *Studia Univ. Babeş-Bolyai Ser. Chemia*
180. C. A. Hutchison Jr., G. A. Candela, *J. Chem. Phys.*, **1957**, *27*, 707.
181. B. Jezowska-Tezebiatowska, *J. Chem. Phys.*, **1963**, *60*, 48.
182. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal Ions*, Clarendon Press, Oxford, **1980**, p. 354.
183. I. Ursu, *Magnetical Resonance of uranium compounds*, Acad. RSR, Bucureşti, **1979**, p. 189.