



*Nikolaev Institute of Inorganic Chemistry  
Russian Academy of Sciences, Siberian Branch  
Novosibirsk*

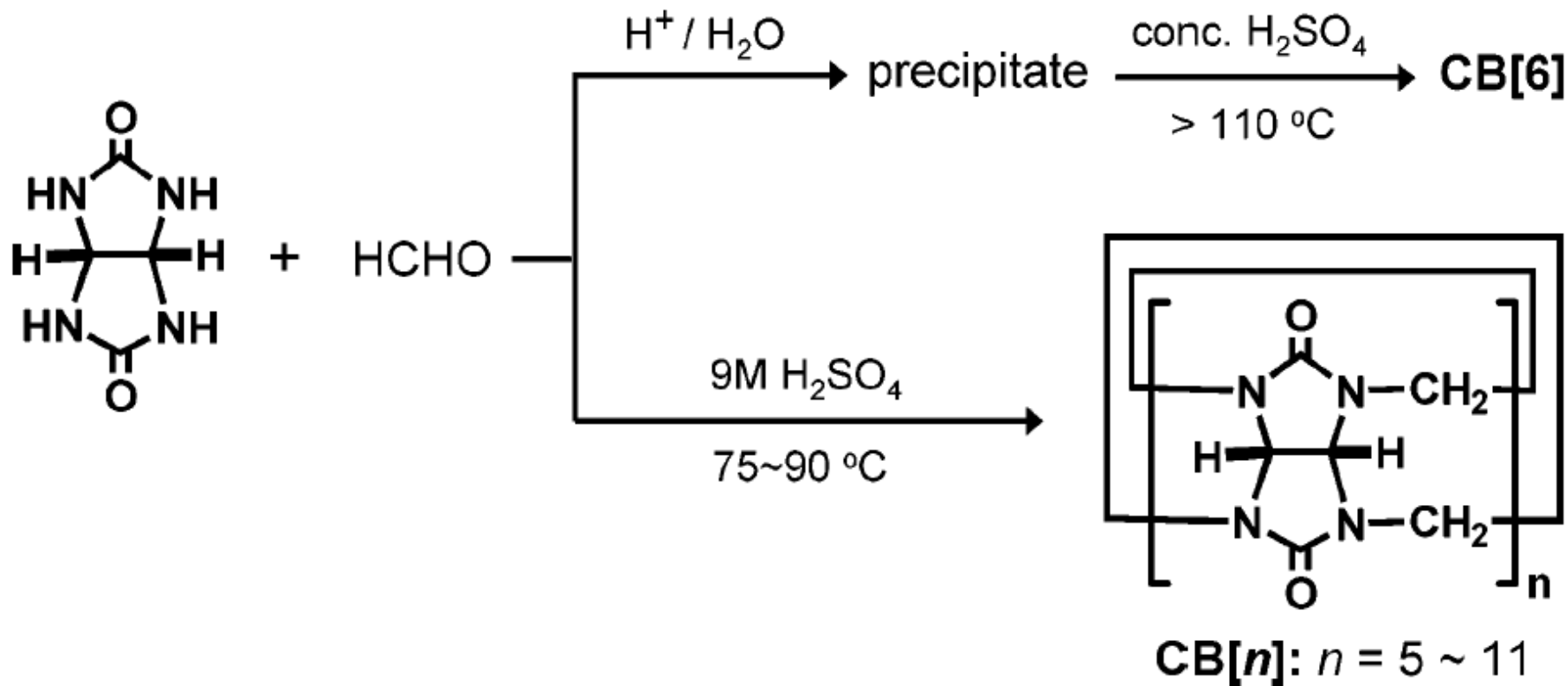
# **Inclusion of metal-organic complexes into cucurbit[8]uril**

**Vladimir P. Fedin, Tatiana V. Mitkina, Olga A. Gerasko**

*Moscow  
2005*



# The cucurbit[n]uril family (CB[n])

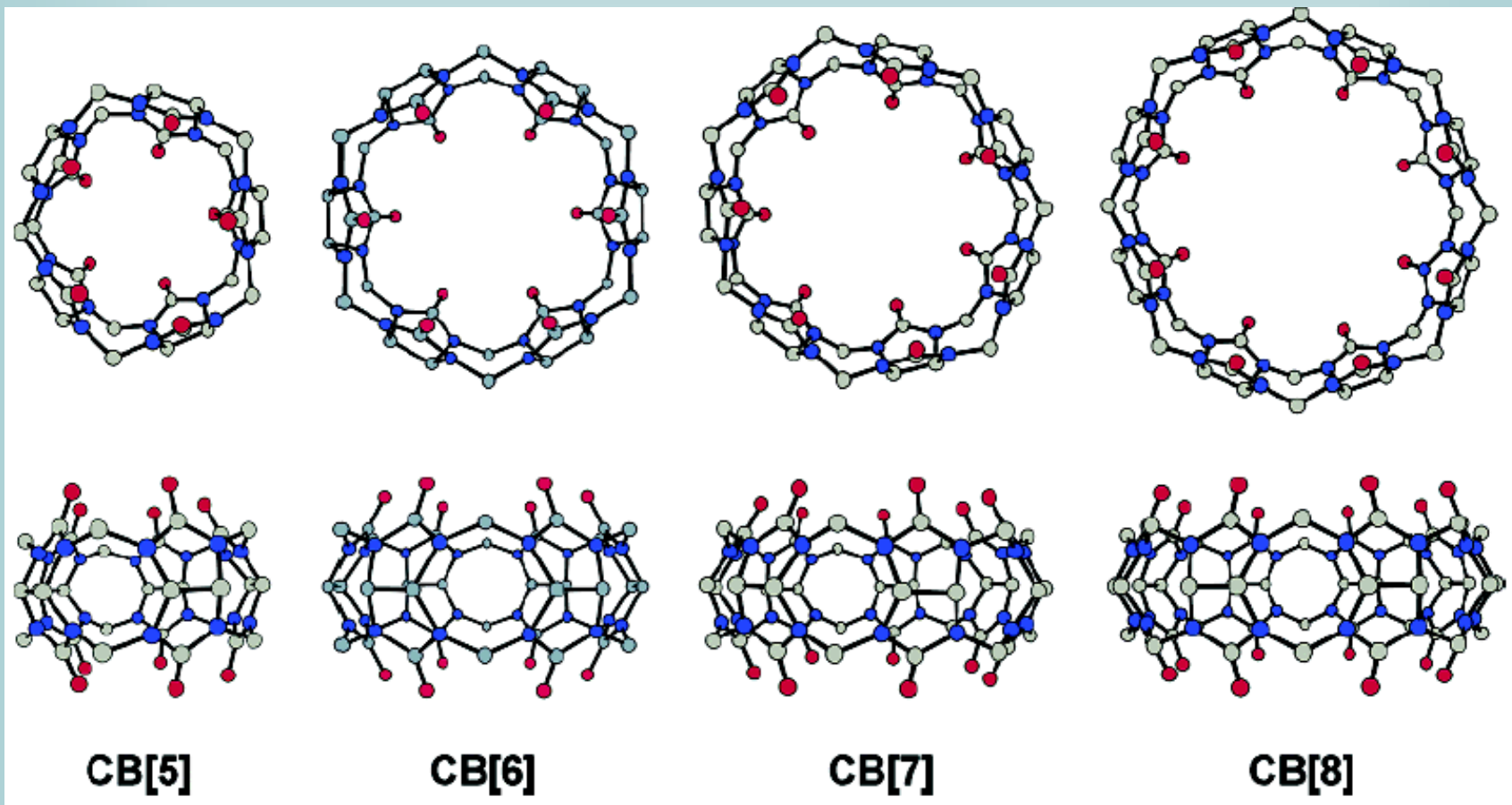


R. Behrend, E. Meyer, F. Rusche, *Liebigs Ann. Chem.* 1905, 339, 1.

W. A. Freeman, W. L. Mock, N. Y. Shih, *J. Am. Chem. Soc.* 1981, 103, 7367.



# The cucurbit[n]uril family (CB[n])



82

164

280

480

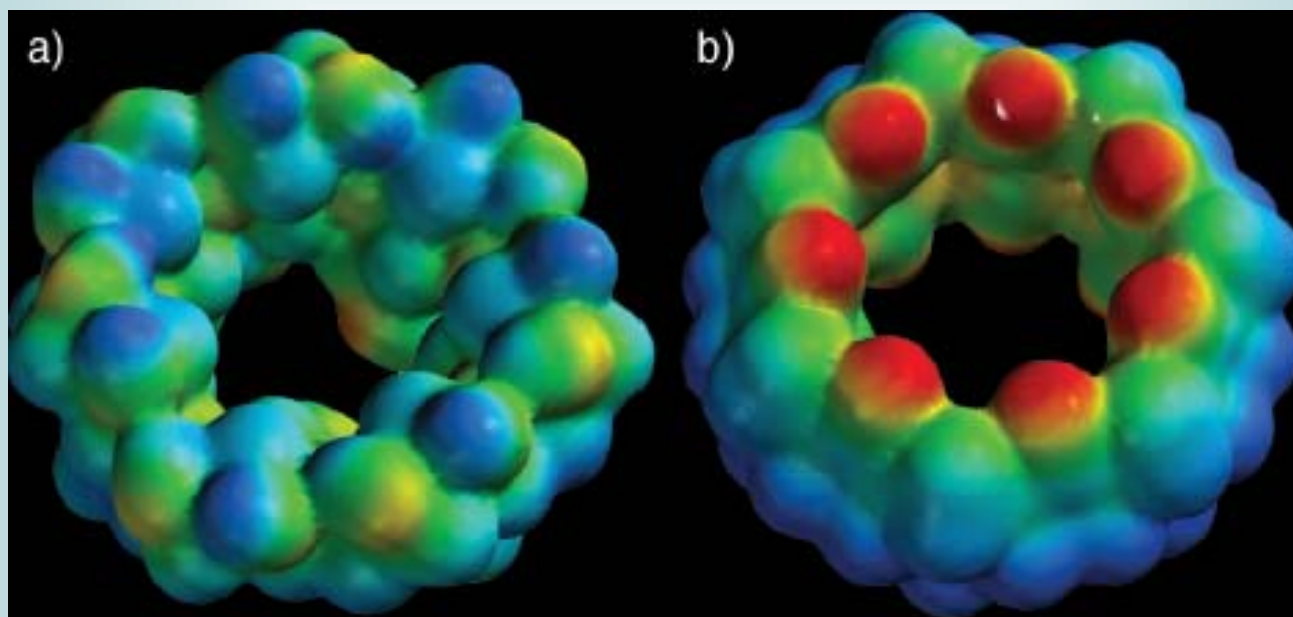
Cavity volume ( $\text{\AA}^3$ )



## Electrostatic potential maps for a) $\beta$ -CD and b) CB[7]

The red to blue color range spans  $-80$  to  $40$  kcal mol $^{-1}$ .

(K. Kim et al., *Acc. Chem. Res.* **2003**, *36*, 621)

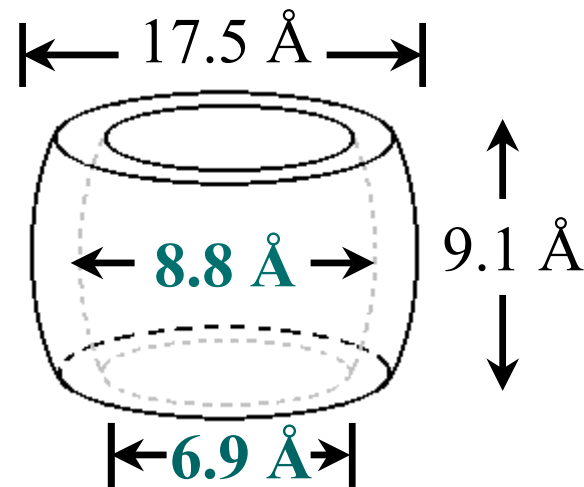
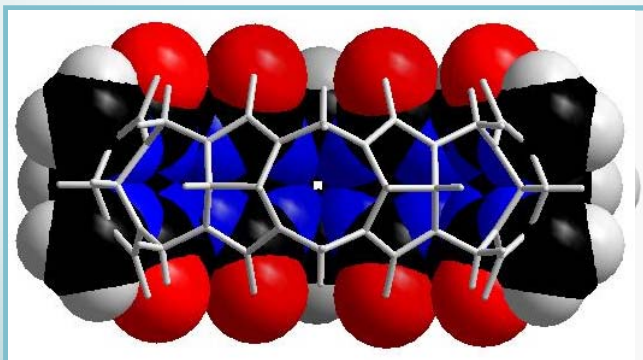
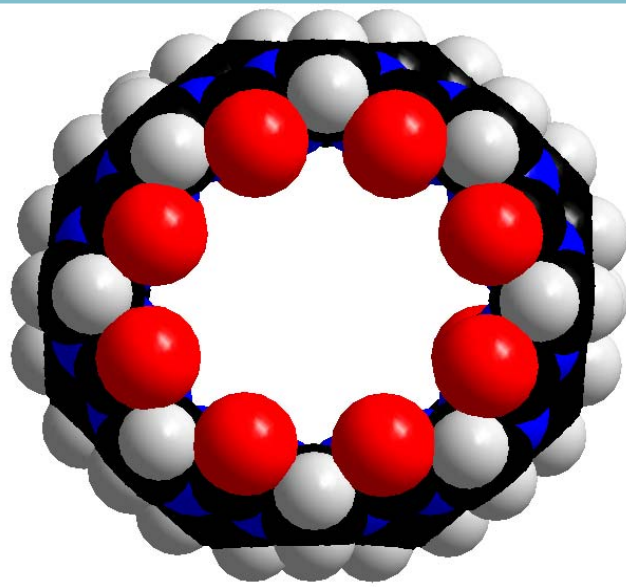
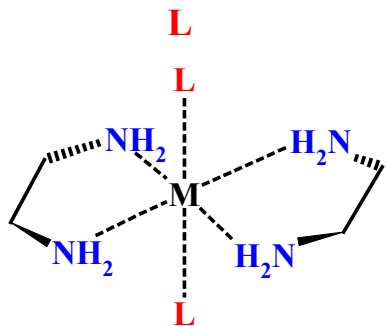
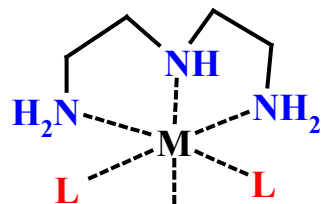
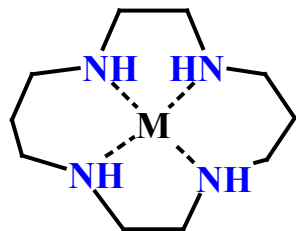


CB[n]s exhibit a pronounced preference to interact with cationic rather than neutral or anionic guests whereas CDs prefer to bind to neutral or anionic rather than cationic guests.



# The cucurbit[n]uril family (CB[8])

## Guests:



dimensions of CB[8]  
molecule

cucurbit[8]uril (CB[8])





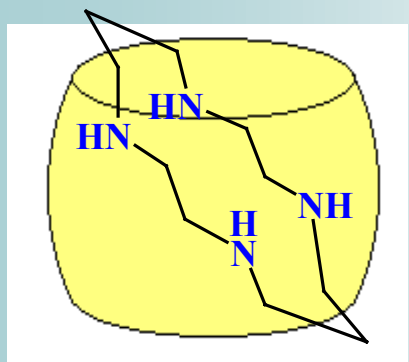
## **Possible approaches to synthesis of inclusion compounds of metal-organic complexes into CB[8]**

- 1) “metal aqua-complex + ligand@CB[8]” scheme**
- 2) direct reaction “host + guest”**
- 3) “guest substitution” approach**



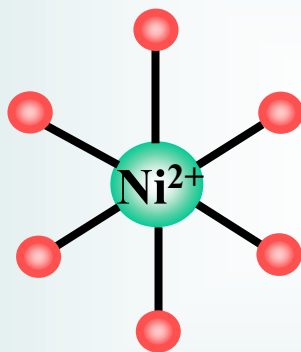
# 1) The approach “metal aqua-complex + ligand@CB[8]”

## Synthesis of $\{[\text{Ni}(\text{cyclam})]@\text{CB}[8]\}\text{Cl}_2 \cdot 16\text{H}_2\text{O}$



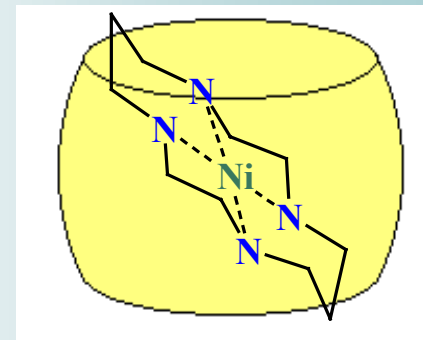
cyclam@CB[8]·  
4HCl·18H<sub>2</sub>O

+



12-fold excess of  
NiCl<sub>2</sub>·6H<sub>2</sub>O

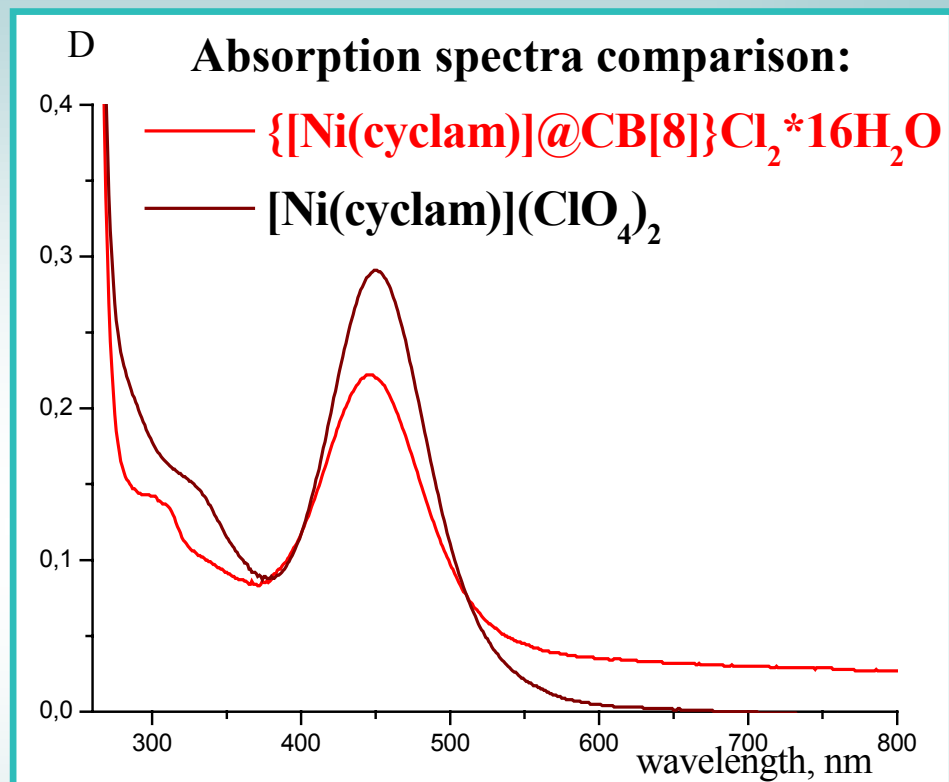
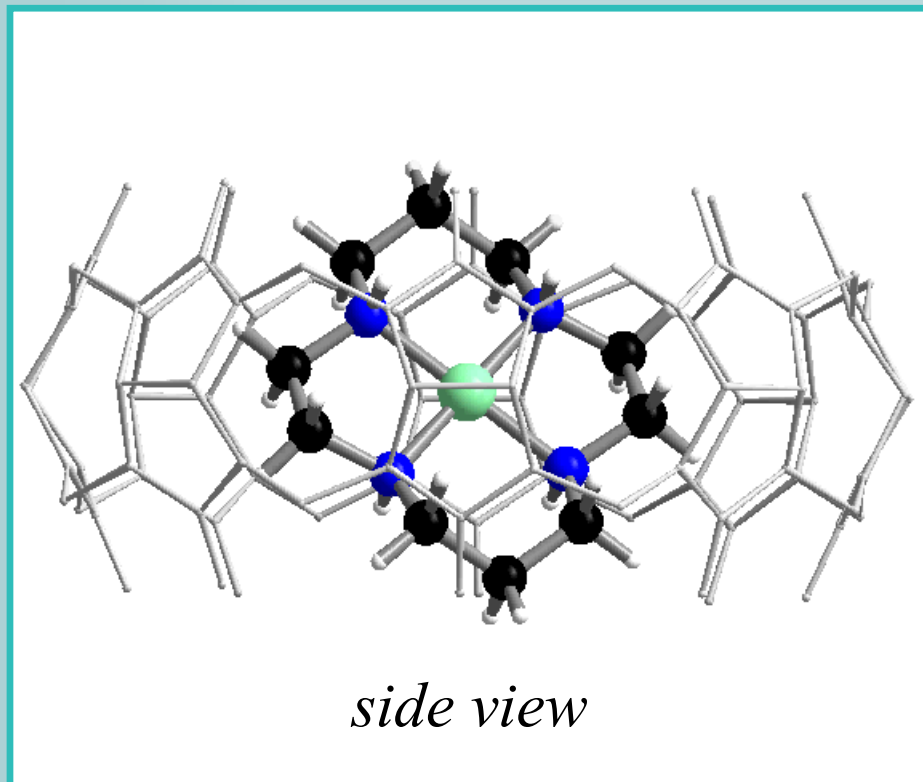
Aqueous  
solution, reflux,  
100°C, 2 h.



yellow crystals,  
yield = 89%,  
hot water soluble



# The structure of $\{[\text{Ni}(\text{cyclam})]@\text{CB}[8]\}\text{Cl}_2 \cdot 16\text{H}_2\text{O}$



□ **ESI-MS:**  $m/z = 793.245$   
 $\{[\text{Ni}(\text{cyclam})] + \text{CB}[8]\}^{2+}$

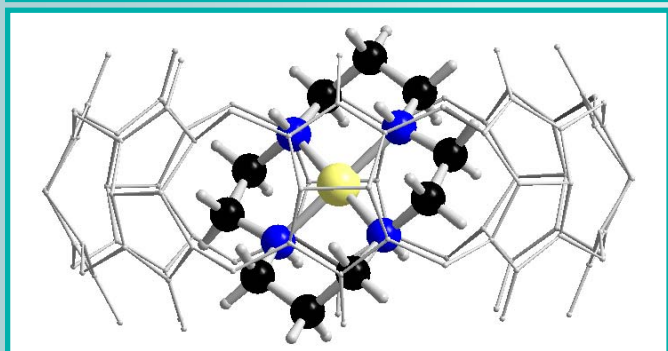
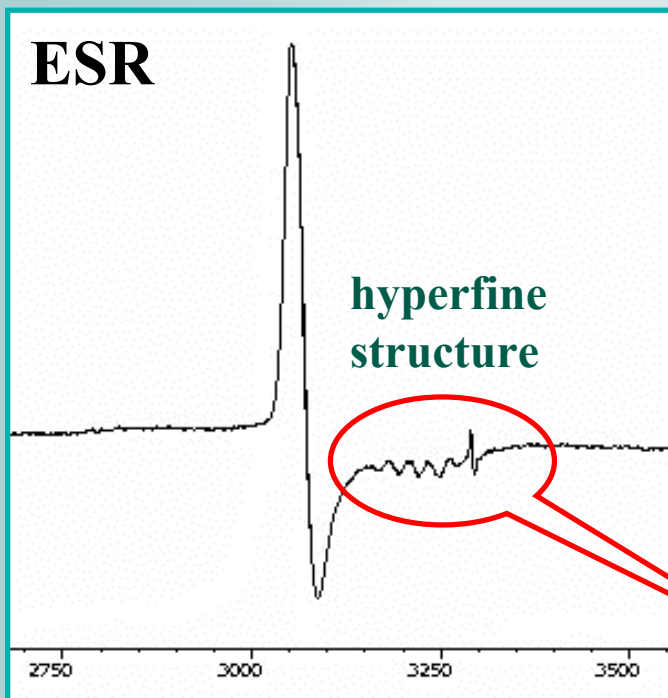
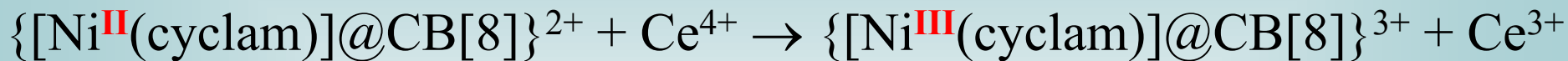
□ **IR:** CB[8] vibrations

□ **X-ray:** square-planar environment of  $\text{Ni}^{\text{II}}$ ; the angle between  $\text{NiN}_4$  plane and equatorial plane of CB[8]  $\angle \sim 70^\circ$



# Ni<sup>II</sup>/Ni<sup>III</sup> oxidation within the CB[8] cavity.

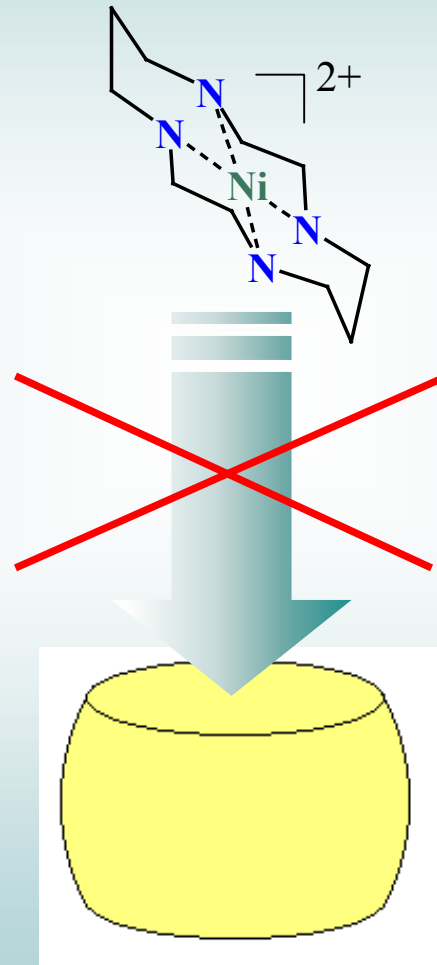
## Synthesis of $\{[\text{Ni}^{\text{III}}(\text{cyclam})]@\text{CB}[8]\}(\text{SO}_4)_{1.5}\cdot 14\frac{2}{3}\text{H}_2\text{O}$



- ❑ **X-ray cryst.:** square-planar environment of Ni<sup>III</sup>; the angle between NiN<sub>4</sub> plane and equatorial plane of CB[8]  $\angle \sim 70^\circ$
- ❑ **IR:** CB[8] vibrations,  $\nu(\text{SO}_4^{2-}) = 1121, 619 \text{ cm}^{-1}$
- ❑ **Solid-state ESR:** low spin ( $S = \frac{1}{2}$ ) d<sup>7</sup> **square-planar Ni<sup>III</sup>N<sub>4</sub> (!)**,  
 $A = 286 \text{ G}$ ,  $g_x = 2.142$ ,  $g_y = 2.277$ ,  
 $g_z = 2.209$ .
- ❑ greenish-yellow crystals, water-insoluble, yield 88%



## 2) Direct approach “host + guest”

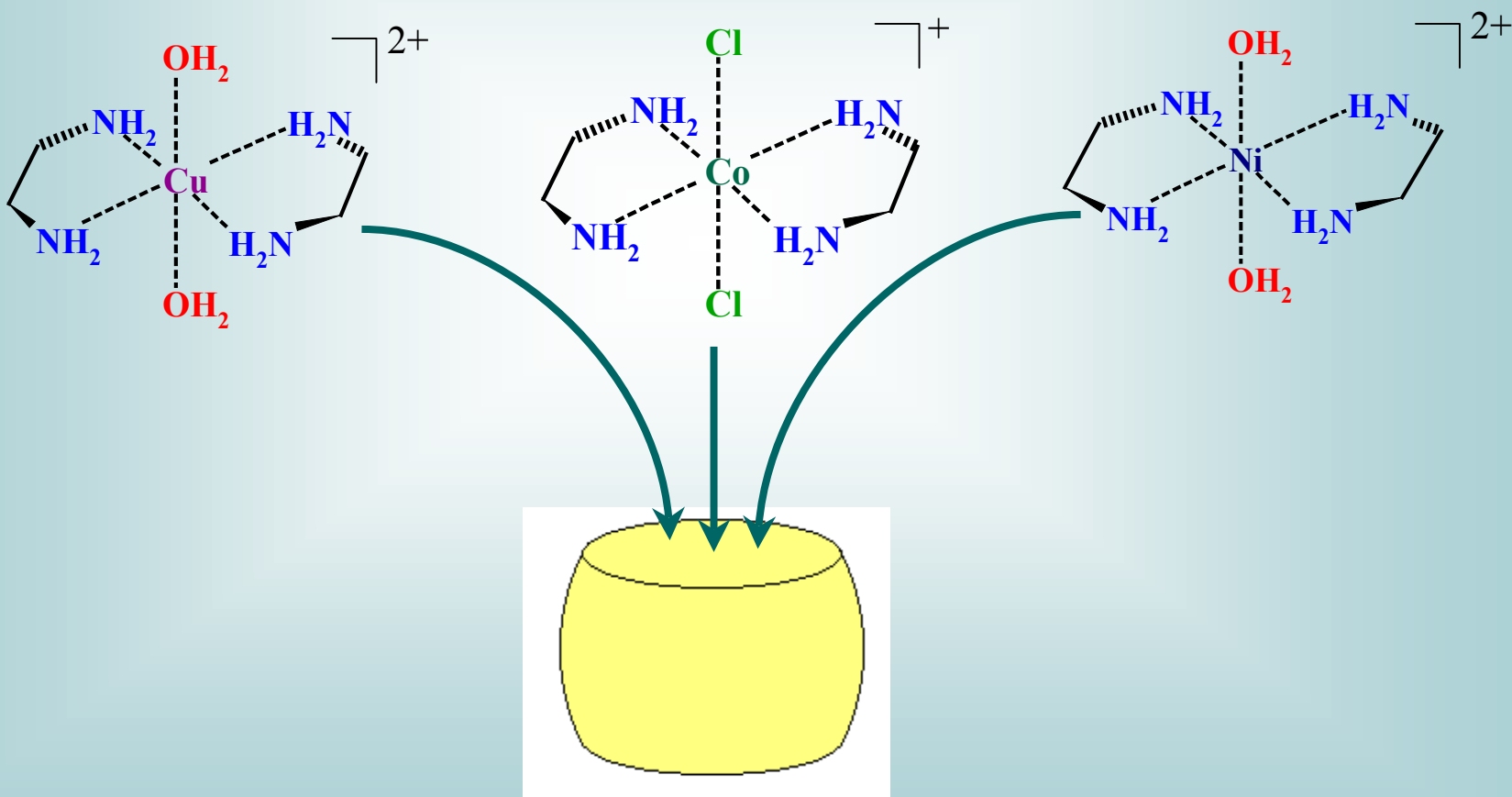


**cucurbit[8]uril**



## 2) Direct approach “host + guest”

Synthesis of  $\{trans-[M(en)_2X_2]@CB[8]\}Cl_n \cdot mH_2O$   
( $M = Cu^{II}, Ni^{III}, Co^{III}$ ;  $X = Cl^-, H_2O$ )



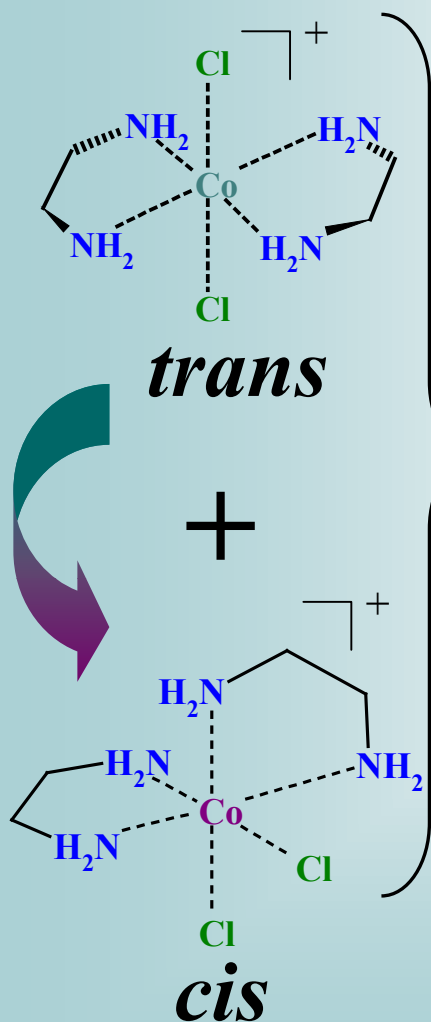
cucurbit[8]uril



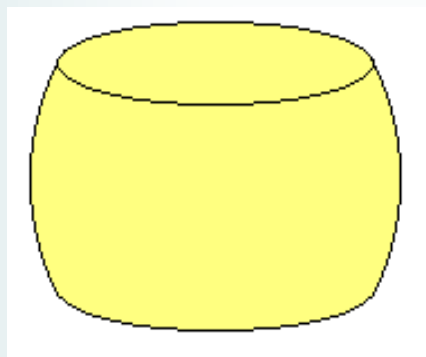
## 2) Direct approach “host + guest”

# Synthesis of $\{trans-[Co(en)_2Cl_2]@CB[8]\}Cl \cdot 17H_2O$

Selective inclusion of *trans*-isomer !

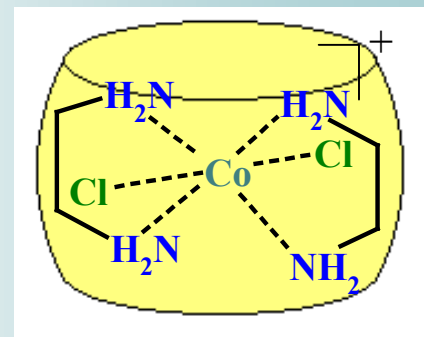


+



CB[8]·20H<sub>2</sub>O

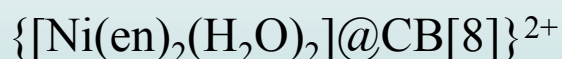
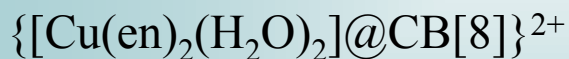
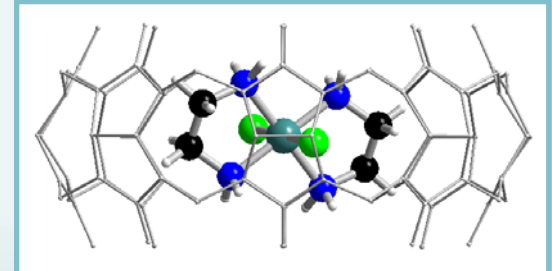
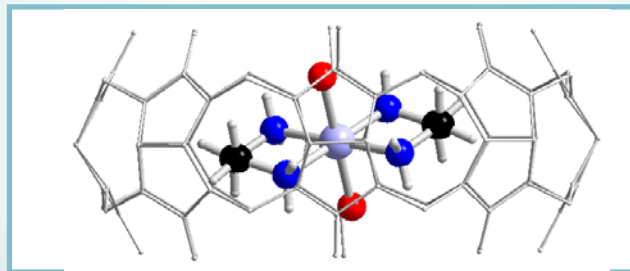
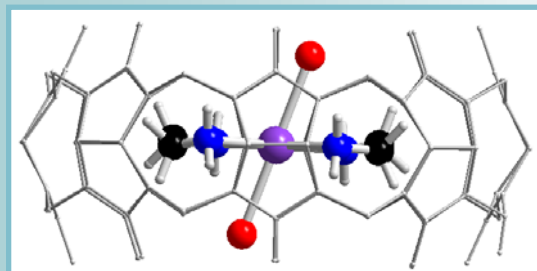
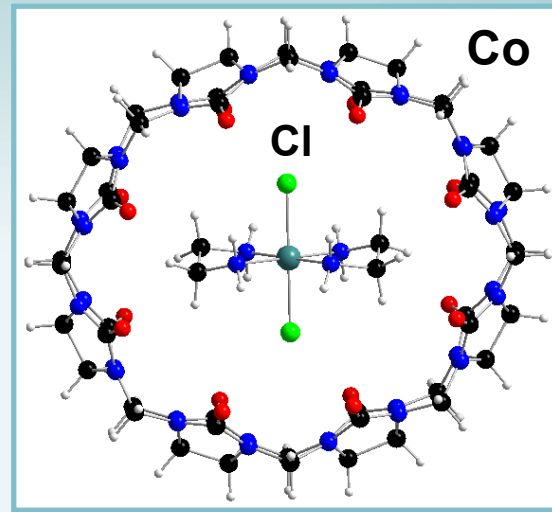
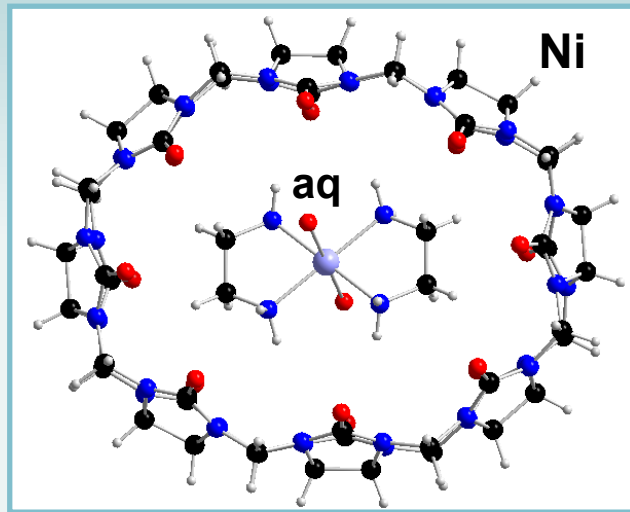
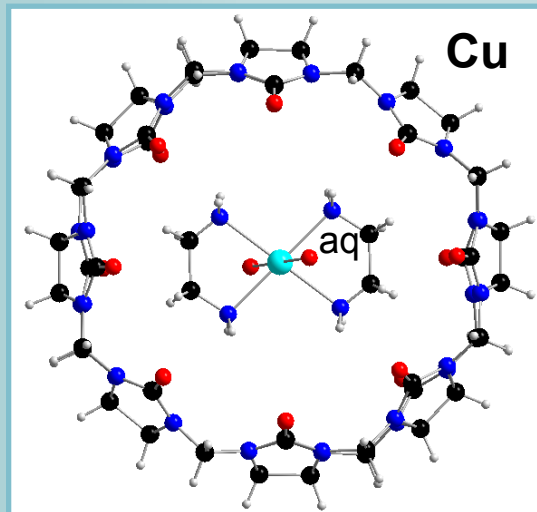
Aqueous solution, reflux, 100°C, 2 h.



dark-green crystals,  
yield = 97%,  
hot water soluble



# Orientations of the ethylenediamine complexes inside the cavity of CB[8]



$$\angle = 0^\circ,$$

$$\text{Cu-N } 2.00 \text{ \AA},$$

$$\text{Cu-O } 2.55 \text{ \AA}$$

$$\angle = 16^\circ,$$

$$\text{Ni-N } 2.10 \text{ \AA},$$

$$\text{Ni-O } 2.13 \text{ \AA}$$

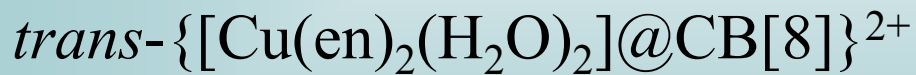
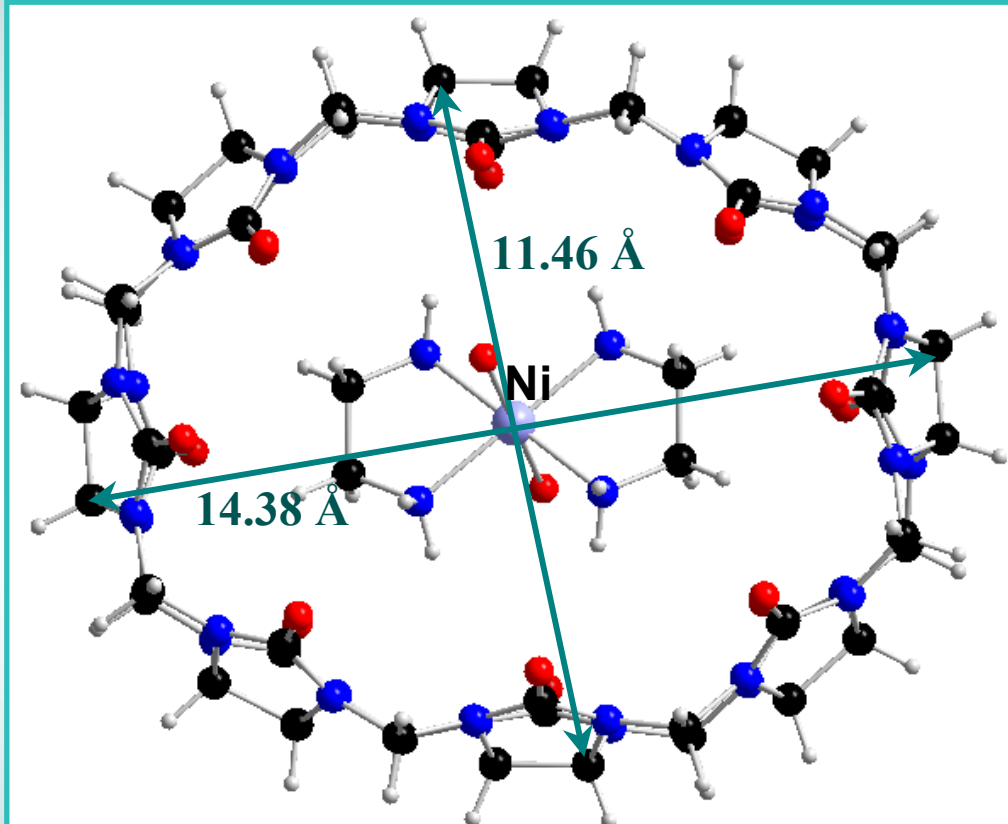
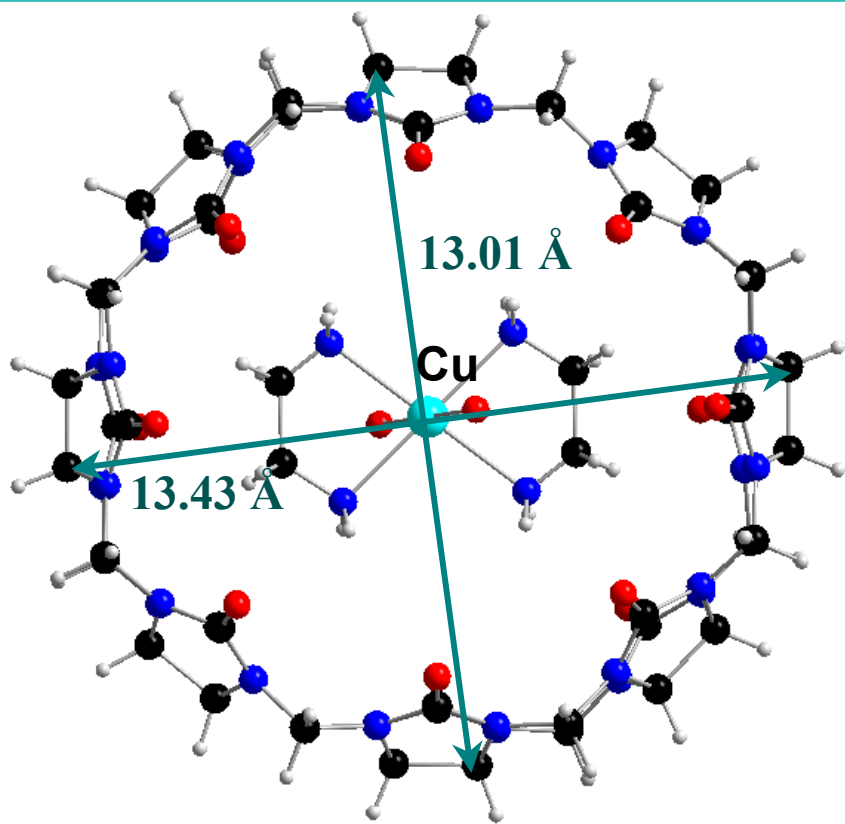
$$\angle = 90^\circ,$$

$$\text{Co-N } 1.92 \text{ \AA},$$

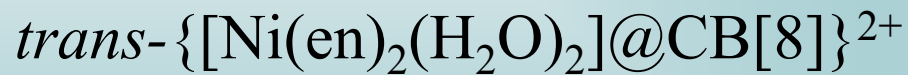
$$\text{Co-Cl } 2.24 \text{ \AA}$$



# Distortion of CB[8] molecule upon encapsulation of guests



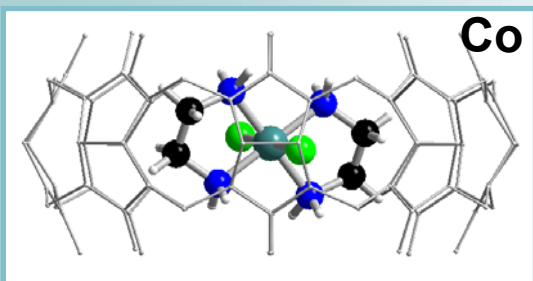
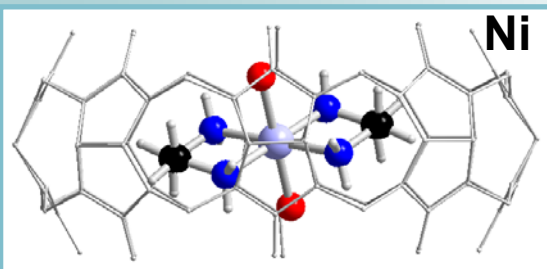
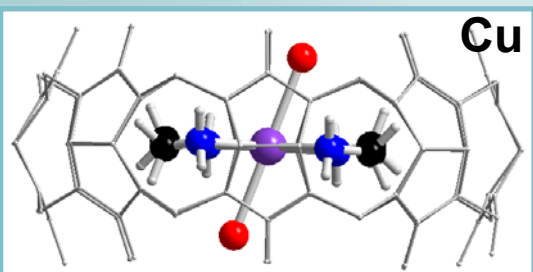
$\Delta\varnothing = 0.42 \text{ \AA} \text{ (Cu-N} = 2.00 \text{ \AA)}$



$\Delta\varnothing = 2.92 \text{ \AA} \text{ (Ni-N} = 2.10 \text{ \AA)}$



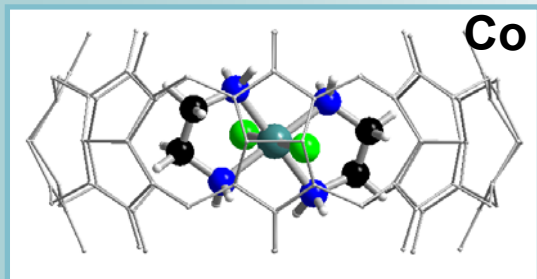
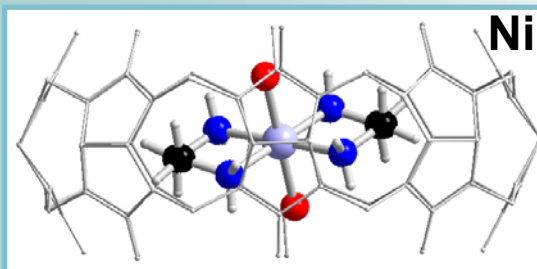
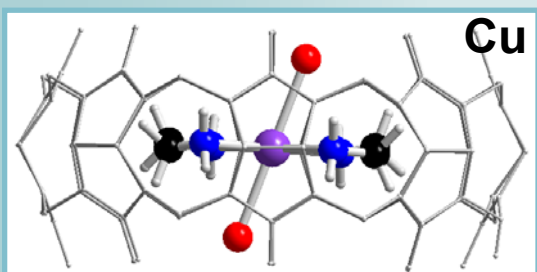
# Solution and solid state studies of $\{trans-$ $[M(en)_2X_2]@CB[8]\}Cl_n \cdot mH_2O$ ( $M = Cu^{II}, Ni^{III}, Co^{III}$ ; $X = Cl^-, H_2O$ )



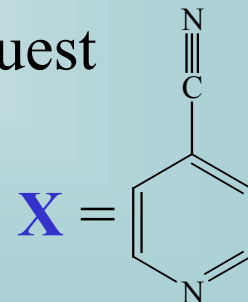
- ❑ X-ray cryst., elemental analysis
- ❑ ESI-MS:  $m/z = 756$   
 $\{CB[8] + Cu(en)_2\}^{2+}$
- ❑ ESR:  $g_{||} = 2.212, g_{\perp} = 2.049$
- ❑ IR: CB[8] vibrations
- ❑ Dissociation upon dissolution in water:  
 $\{[Cu(en)_2(H_2O)_2]@CB[8]\}^{2+} \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + CB[8]$



# Solution and solid state studies of $\{trans-$ $[M(en)_2X_2]@CB[8]\}Cl_n \cdot mH_2O$ ( $M = Cu^{II}, Ni^{III}, Co^{III}$ ; $X = Cl^-, H_2O$ )

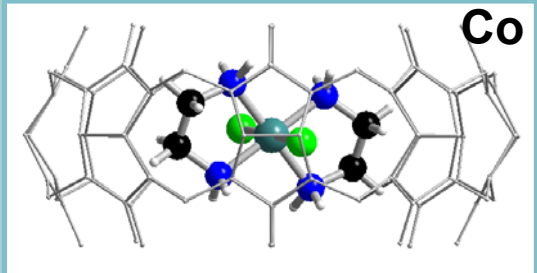
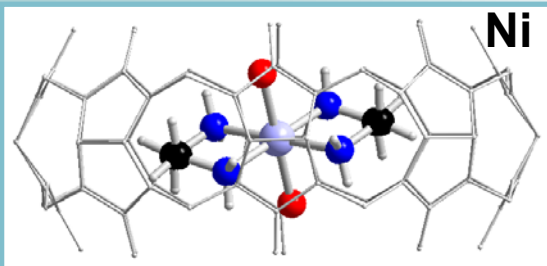
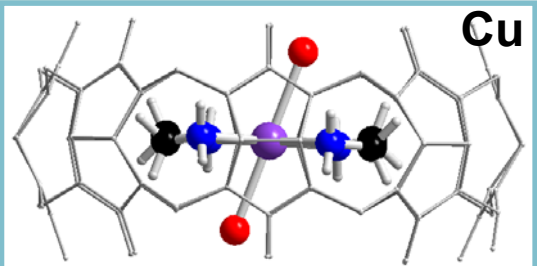


- ❑ X-ray cryst., elemental analysis
- ❑ ESI-MS:  $m/z = 510$   
 $\{CB[8] + Ni(en)_2 + Na\}^{3+}$
- ❑  $^1H$  NMR: CB[8] resonances became broadened and en signals disappeared upon inclusion
- ❑ IR: CB[8] vibrations
- ❑ Stable in solution
- ❑ May undergo reactions of guest substitution

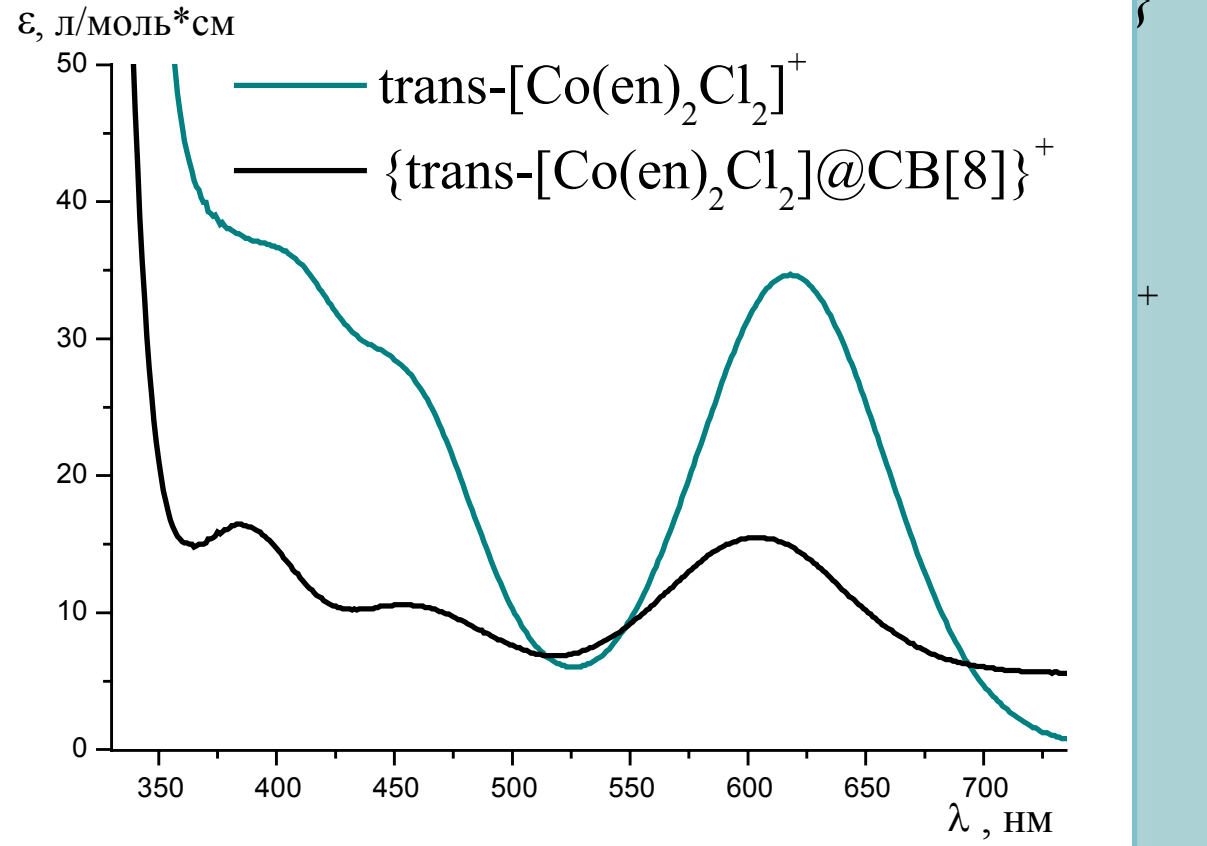




# Solution and solid state studies of $\{trans-[M(en)_2X_2]@CB[8]\}Cl_n \cdot mH_2O$ ( $M = Cu^{II}, Ni^{II}, Co^{II}$ ; $X = Cl^-, H_2O$ )

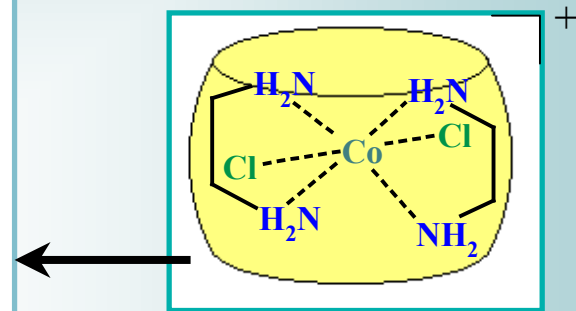
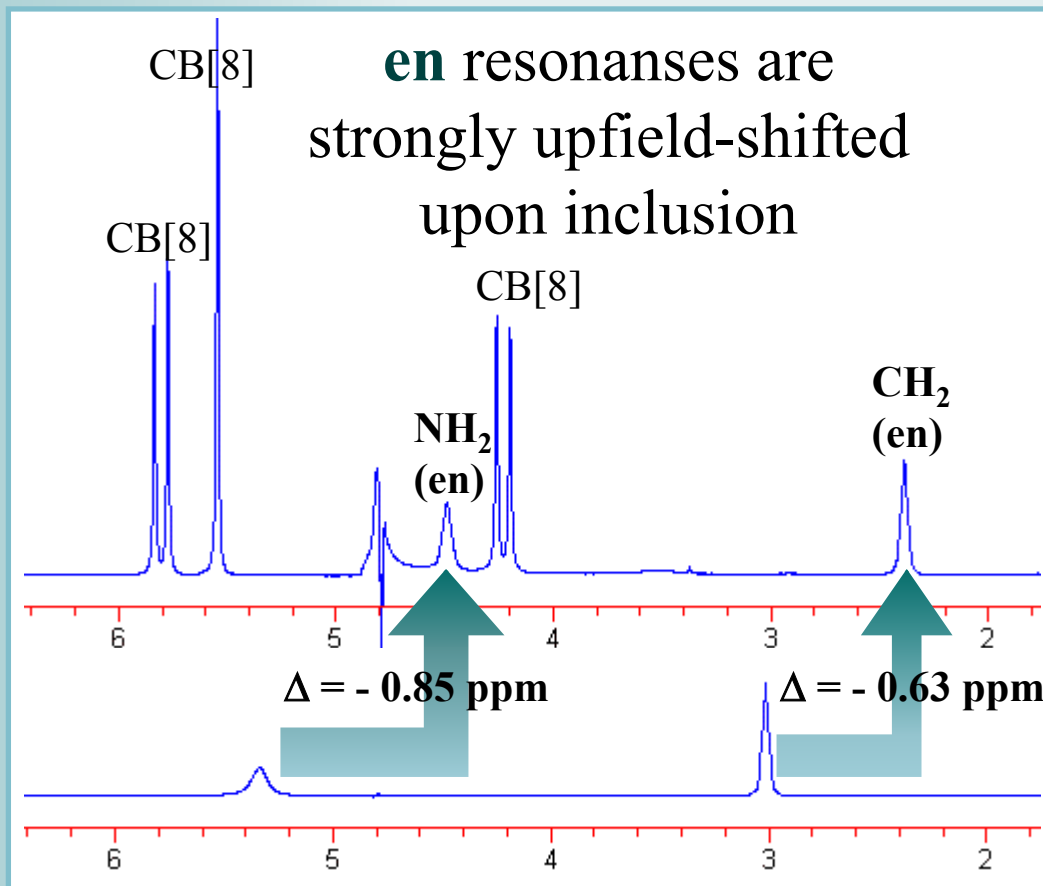


Absorption spectra comparison: **hypsochromic schift** upon inclusion

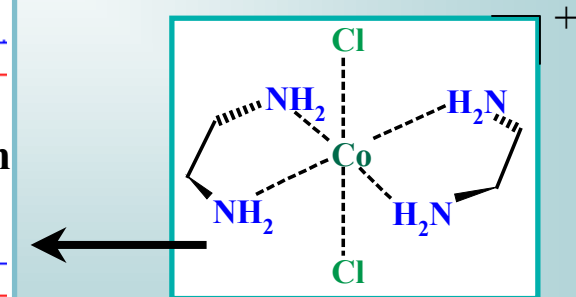




# $^1\text{H}$ NMR-spectra comparison of $\text{D}_2\text{O}$ solutions of $[\text{trans-Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and $\{[\text{trans-Co}(\text{en})_2\text{Cl}_2]@\text{CB}[8]\}\text{Cl}\cdot 17\text{H}_2\text{O}$



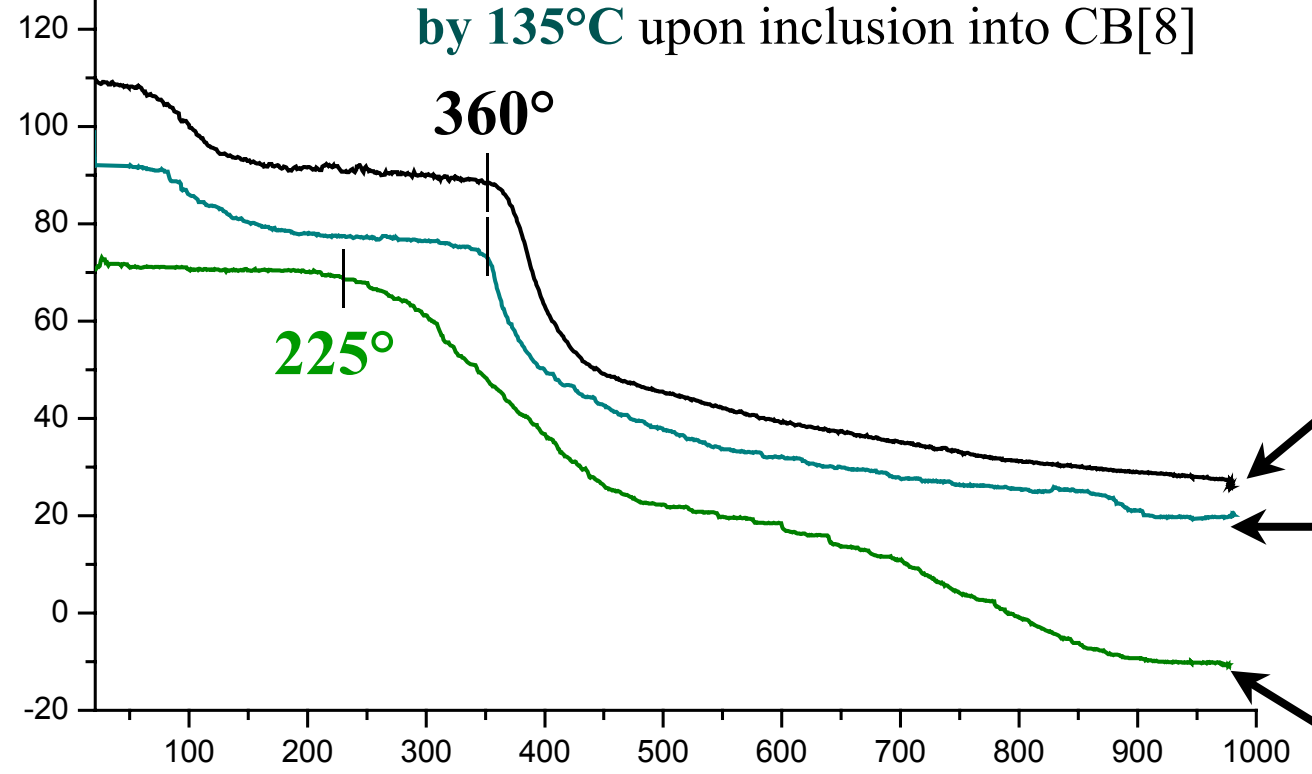
*inclusion compound*



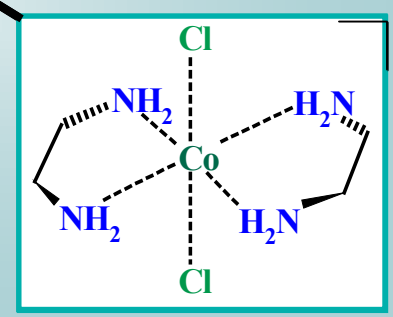
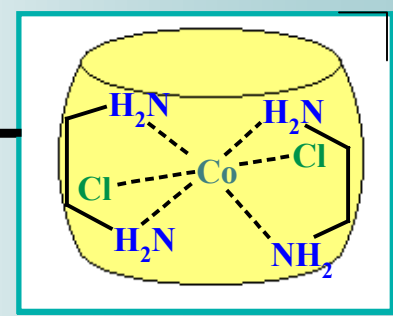
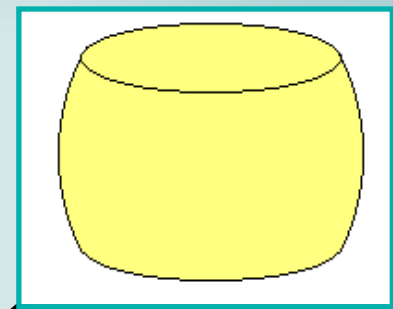
*original complex*

# Thermogravimetric data for $\{[trans-Co(en)_2Cl_2]@CB[8]\}Cl \cdot 17H_2O$ , $trans-[Co(en)_2Cl_2]Cl$ and $CB[8] \cdot 17H_2O$ samples

TG, mg T(decomposition of  $trans-[Co(en)_2Cl_2]Cl$ ) increased by  $135^\circ C$  upon inclusion into CB[8]



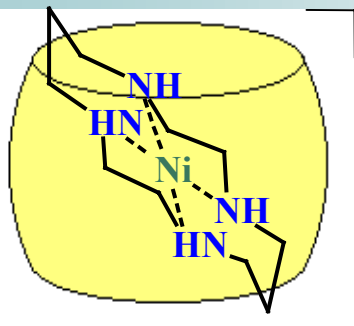
- $trans-[Co(en)_2Cl_2]@CB[8]\}Cl \cdot 17H_2O$
- $CB[8] \cdot 17H_2O$
- $trans-[Co(en)_2Cl_2]Cl$





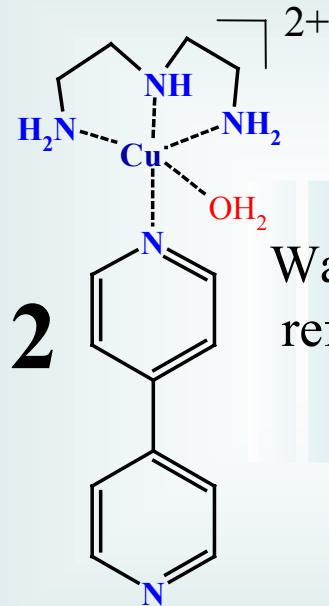
### 3) "Guest substitution" approach

## Synthesis of

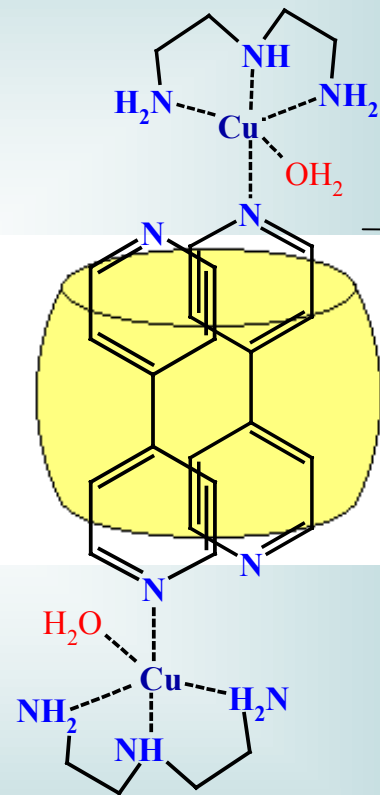


2+

+



Water solution,  
reflux, 100°C,  
3 h.



4+

+



2+

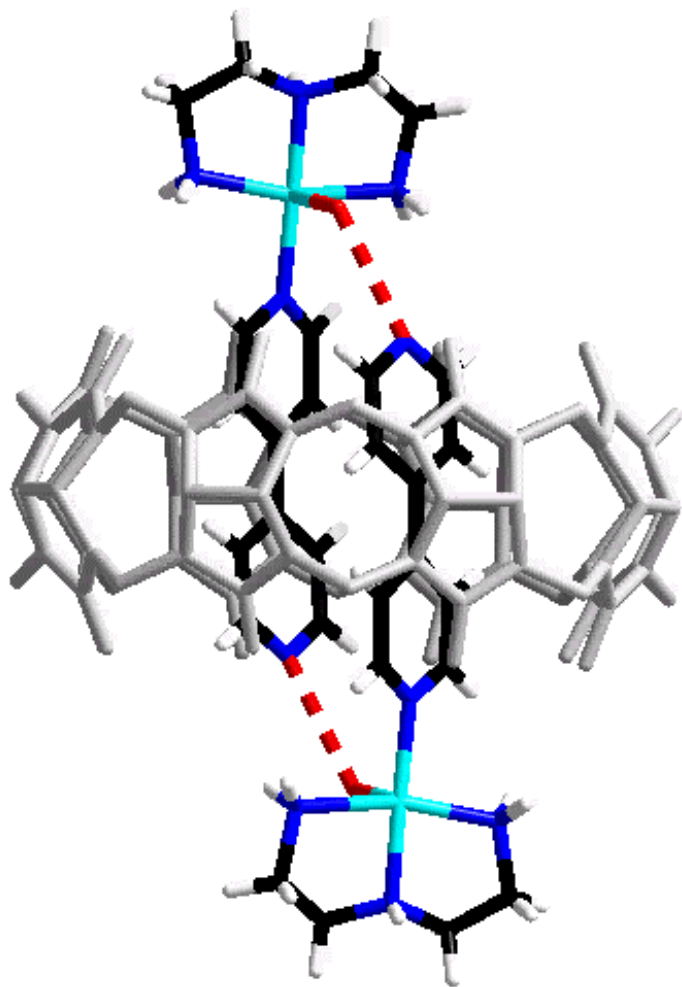
$\{[\text{Ni}(\text{cyclam})]@ \text{CB}[8]\} \text{Cl}_2 \cdot 16\text{H}_2\text{O}$

10-fold excess of  
 $[\text{Cu}(\text{dien})(4,4'\text{-bipy})$   
 $(\text{H}_2\text{O})](\text{ClO}_4)_2$

Violet crystals, yield 60%



# The X-ray crystal structure of $\{[\text{Cu}(\text{dien})(4,4'\text{-bipy})(\text{H}_2\text{O})]_2@ \text{CB}[8]\}(\text{ClO}_4)_4 \cdot 11\text{H}_2\text{O}$



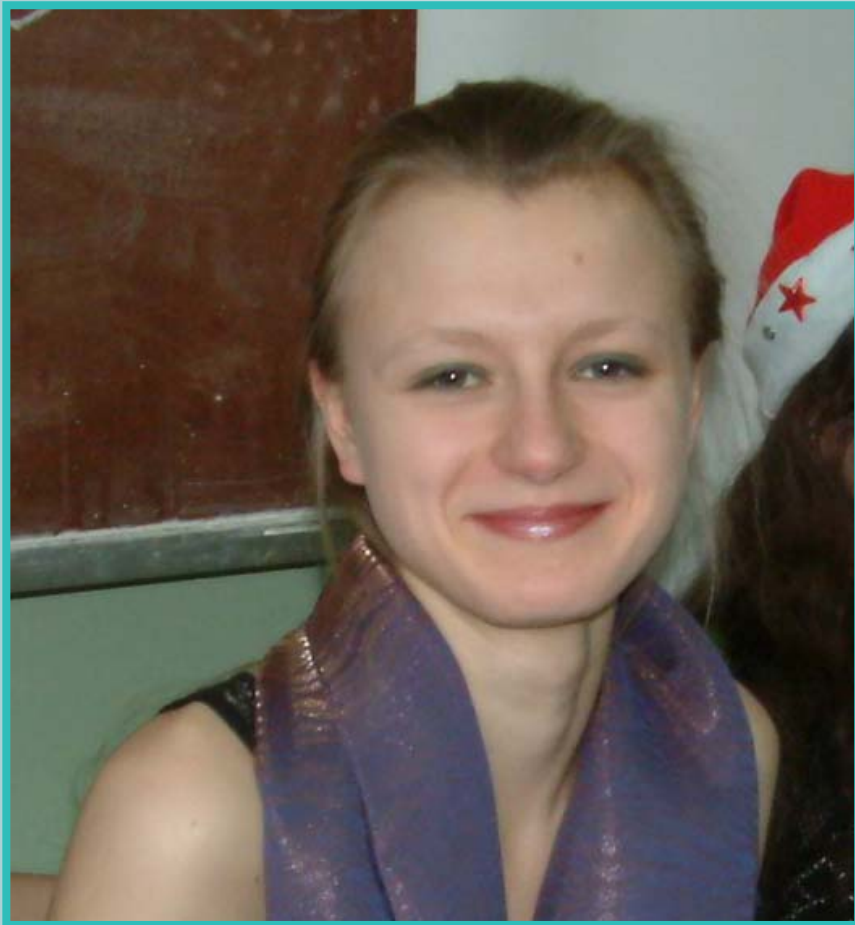
- ❑ X-ray cryst. structure, elemental analysis
- ❑ Absorption spectra:  $\lambda$  ( $\epsilon$ ): 600 (185), 270 (sh), 240 (46200) (=  $\lambda$ ,  $\neq \epsilon$  of free guest)
- ❑ ESI-MS:  $m/z = 825.8$   
 $\{\text{CB}[8] + \text{Cu}(\text{dien})(4,4'\text{-dipy})\}^{2+}$
- ❑ Solid-state ESR:  $g_z = 2.312$ ,  $g_x = g_y = 2.045$  ( $g_{\parallel} = 2.24$ ,  $g_{\perp} = 2.06$  for free guest) – Cu-OH<sub>2</sub> become longer
- ❑ IR: vibrations of CB[8],  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  4,4'-dipy,  $\delta(\text{R}_2\text{N}-\text{H})$  dien,  $\nu(\text{ClO}_4^-)$



## Conclusions

Inclusion into the cavity of cucurbit[8]uril may be helpful for:

- 1) isolation of metal complexes with unusual oxidation states and coordination environments
- 2) stabilization of guest complexes in solid state and in solution towards thermolysis, isomerization etc.



**Tatiana V. Mitkina**



**Dr. Olga A. Gerasko**



# Acknowledgement

- ❑ **RFBR**
- ❑ **INTAS (Prof. F. Secheresse)**
- ❑ **RAS Target Programme (Prof. A.I. Kononov)**

