The Development of Primary Explosives in China

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Resume

- **Date of birth: Feb. 25, 1960**
- **Position: Full professor, Ph. D Advisor**

  Beijing Institute of Technology
- **Education:**

  1978.10-1982.7 diploma Bachelor,

  1988.9-1990.7 Master of Science,

  1990.9-1993.3 Ph. D.

  Nanjing University of Science and Technology

  1993.3-1995.3 Postdoctoral fellowship

  Beijing University of Science and Technology

Brief Introduction

Researching Areas:

Mainly on Primary explosive for civil application and ammunitions

Include: Energetic coordination compound, energetic salts, preparation, manufacture, characterization, analysis, test, et al works around these areas.

- **Awards: National Invention Award, 2nd, one**
- **National Defense Project Awards, 2nd, Two, 5rd, two**
- **Government Award Allowances in 2005**

  Excellent MS and Ph. D. Owner of Defense Industrial in 2005
- **Invention patent 22**
- **Publications: more than 300, 《SCI》, 《EI》 and 《ISTP》 cited more than 200**

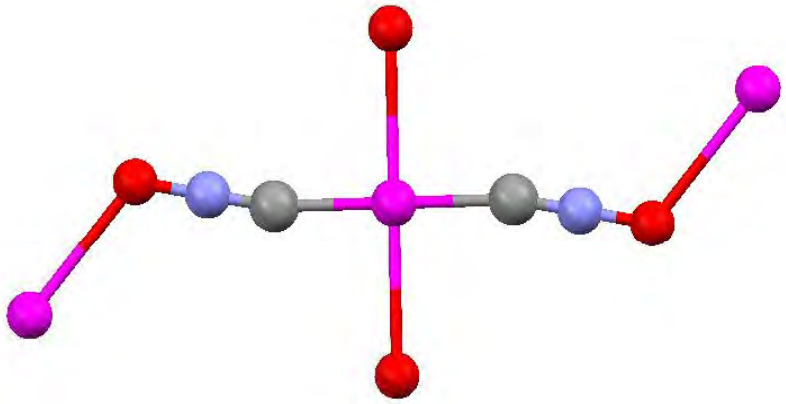
The foundations

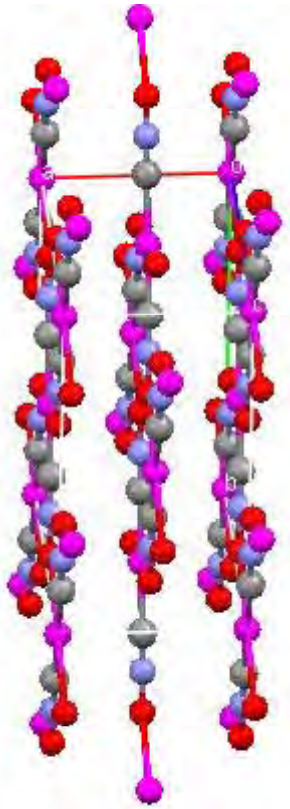
- During the second world wide war
- Anti-Japanese war
- Black gun powder

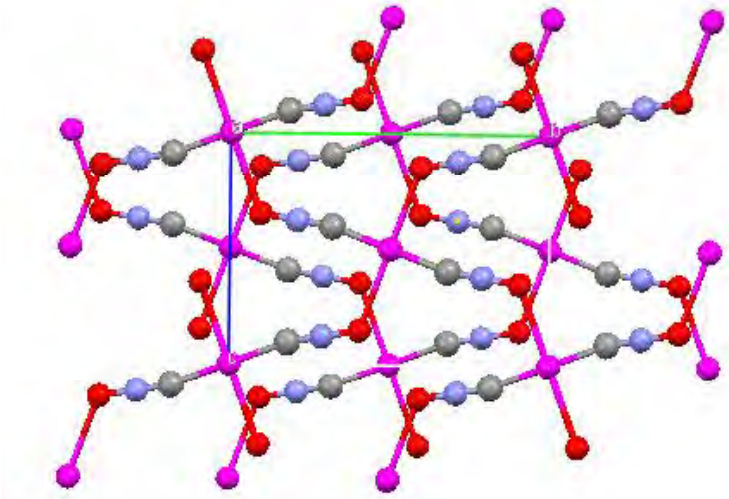
past

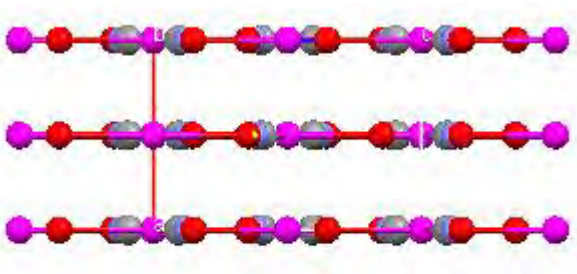
$Hg(ONC)_2$

Mercury Fulminate









The Foundations

- **Mercury Fulminate**
- **It was manufactured in valley, beach of river for safety**
- **Used for ammunitions and mining**

The Foundations

- **Since the New China established**
- **Imported technology from the former Soviet Union**
- **Industrial conditions and scale up to production line**
- **Mining cap loading and ammunitions**

Properties

- Easy to be manufactured
- Easy to use in caps
- Good application properties in percussion composition, stab composition
- Sensitive to friction, percussion and flame

Drawback

- **Mercury toxicity**
- **waste water pollution environmental heavily**
- **Incompatible with aluminum**
- **The Mercury pollution is the main concerns now, and it is given up in China from 1990's totally**

Now 1 Lead Azide

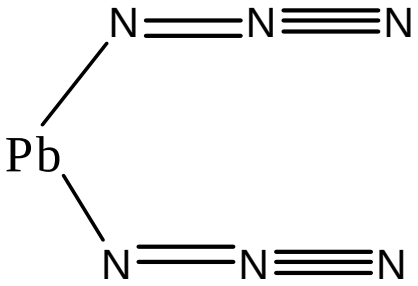
Main Primary explosive on the World

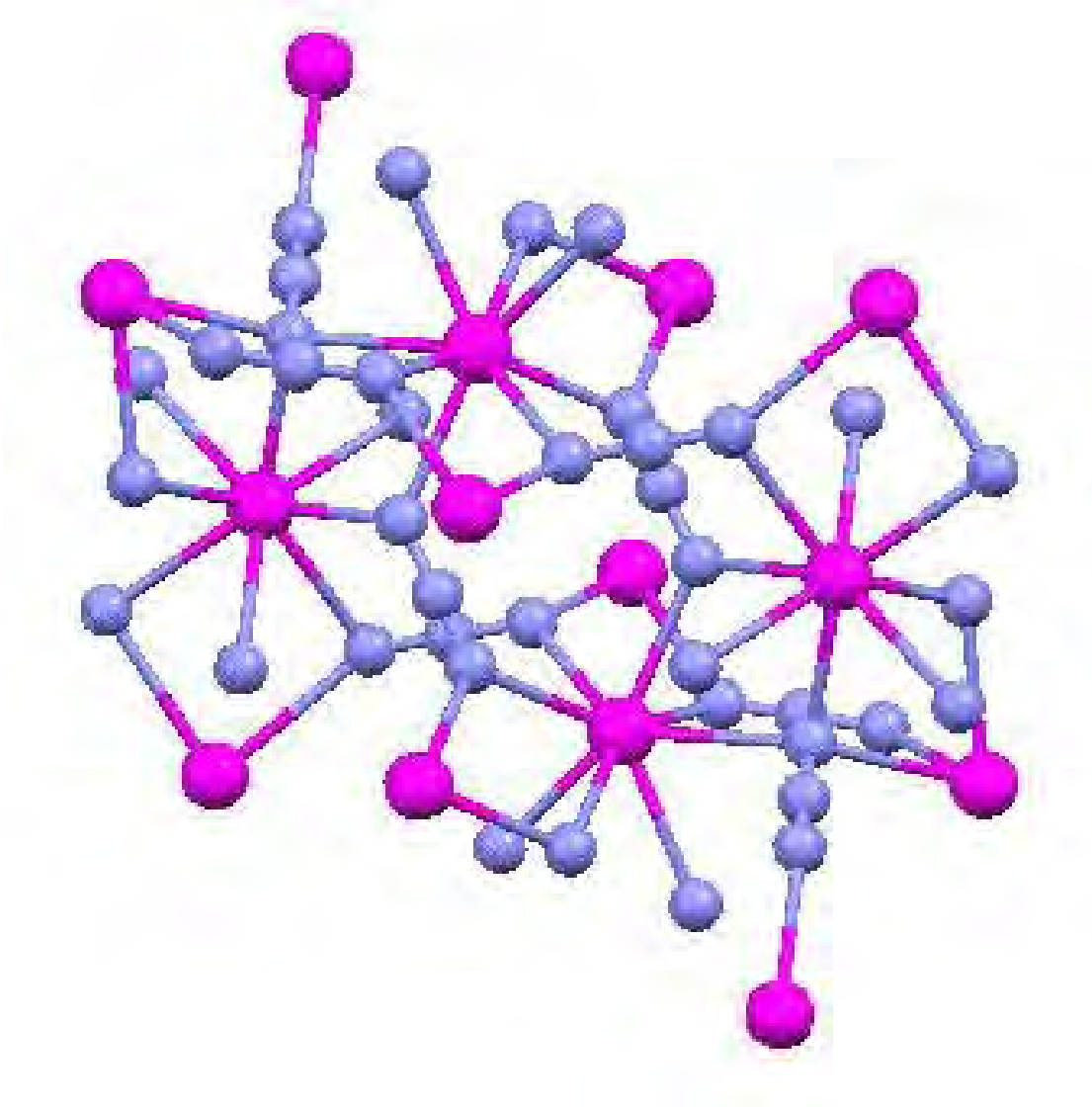
A series of products of Lead azide with different modifiers

No new compounds can exceed LA on DDT process

Structure

$Pb(N_3)_2$





Properties

- **High friction, high weight drop sensitivities**
- **Low flame sensitivity**
- **Good stability and tolerance with temperature**

Characteristics

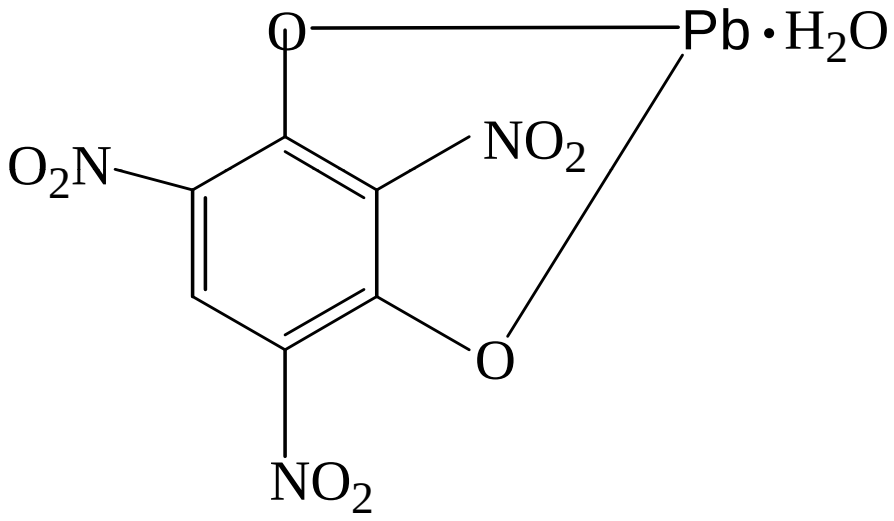
- The most powerful, the shortest DDT length
- The lowest loading for initiating of RDX
- The loading weight is as low as 5 to 10mg for initiating RDX in tiny detonator
- It is still the most powerful primary explosive in the world

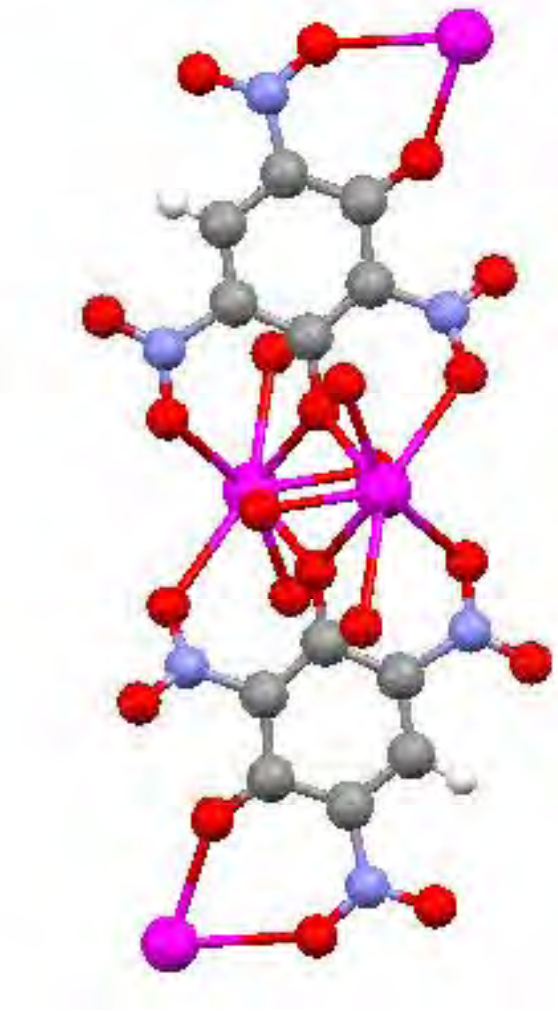
Drawbacks

- **Bad compatible with copper, copper containing alloy and RDX**
- **One of the raw material is NaN_3, acute toxicity to human, as KCN !**
- **Waste water contain azide, heavy metal lead**

Now 2 Flammable King

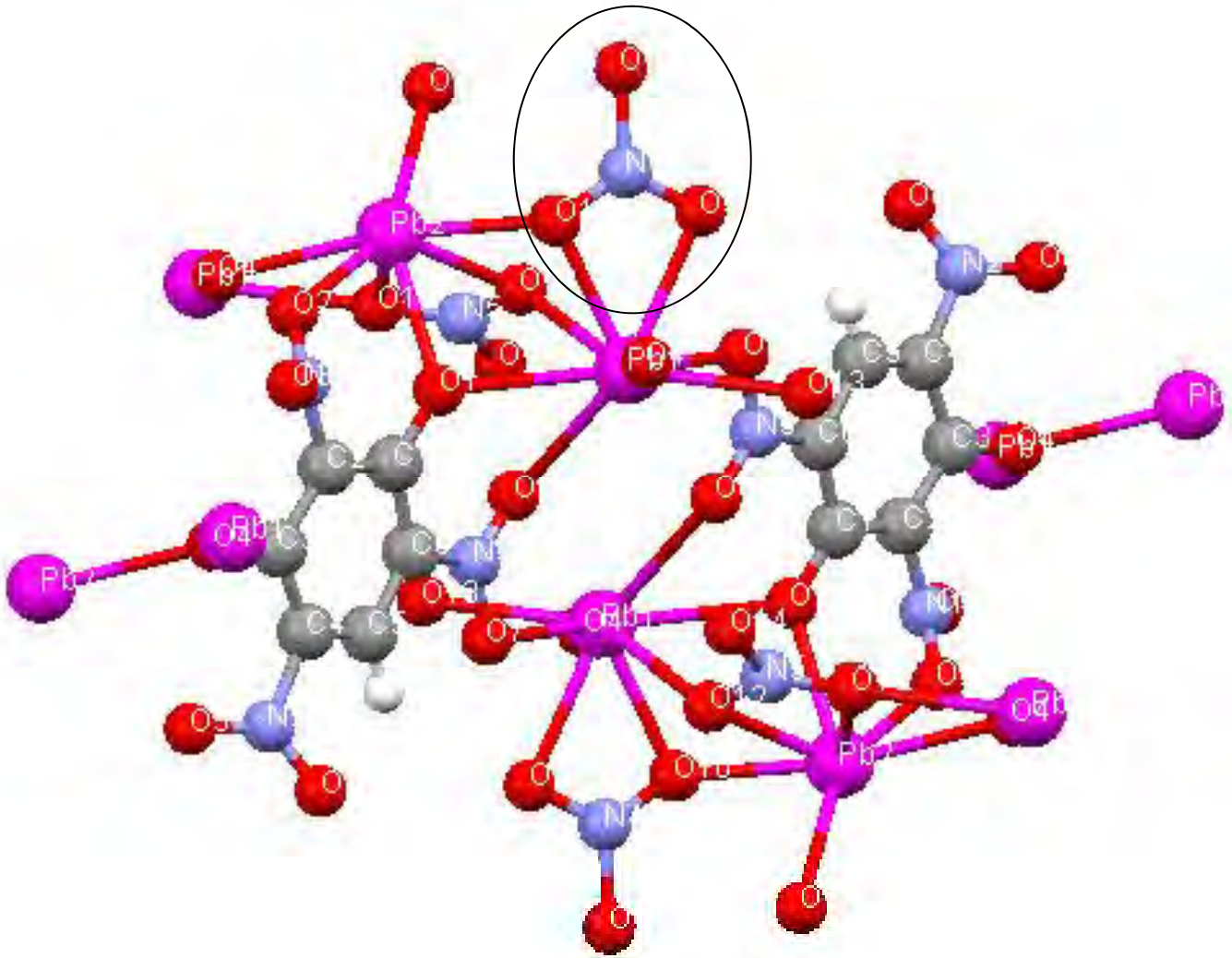
Lead Trinitroresorcinate



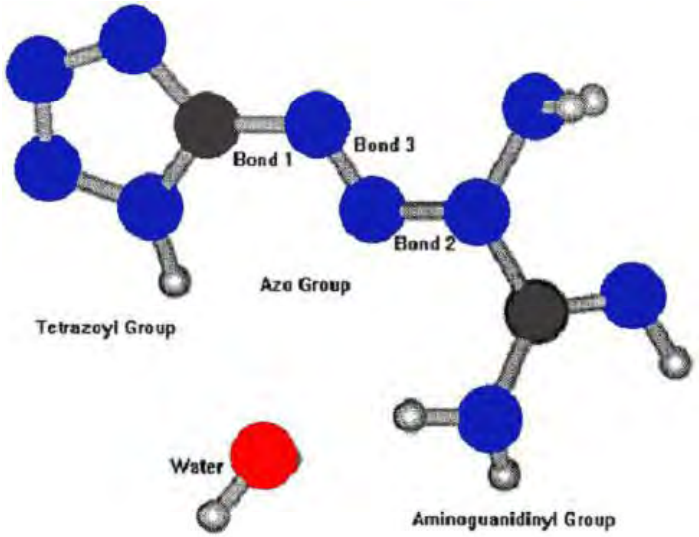


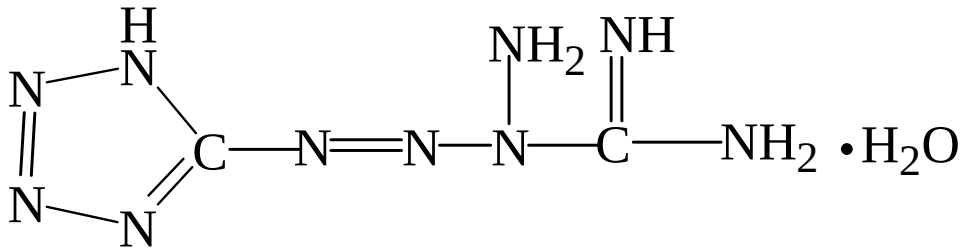
1. **Easy flammable and easy igniting**
2. **Highest static electric sensitivity**
3. **Low output for initiating ability for secondary explosives**

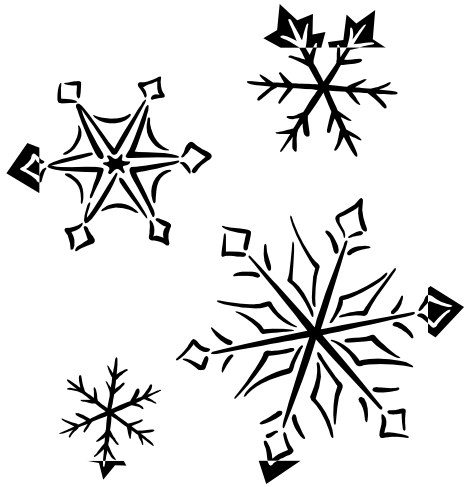
$\{Pb_2(TNR)(NO_3)(H_2O)\}_n$



Now 3 The excellent sensitizer Tetrazene





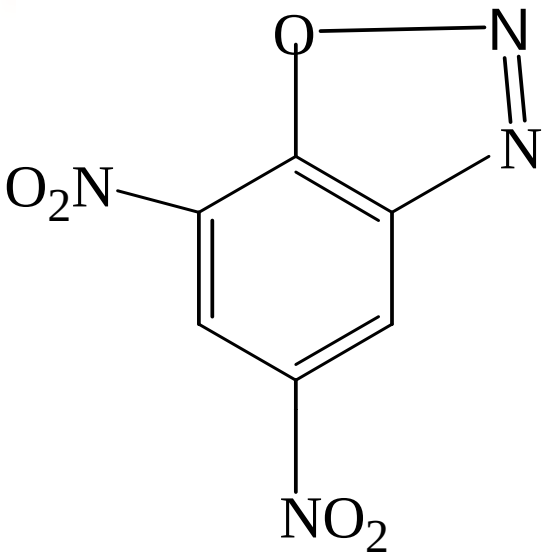


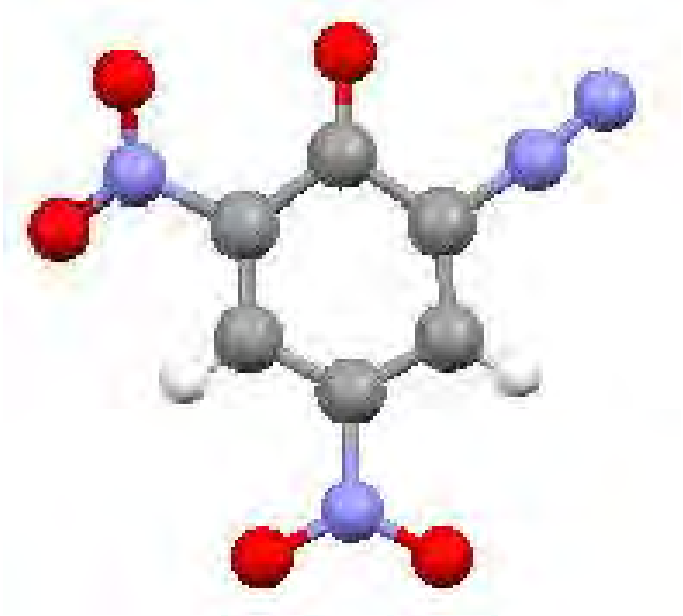
1. Mainly used as composition in mixture composite

2 It is very low thermal stability with decomposition point as low as 114℃.

3 bad flowing ability, low output, and can’t be used in singly

Now 4 Pollution Maker——DDNP





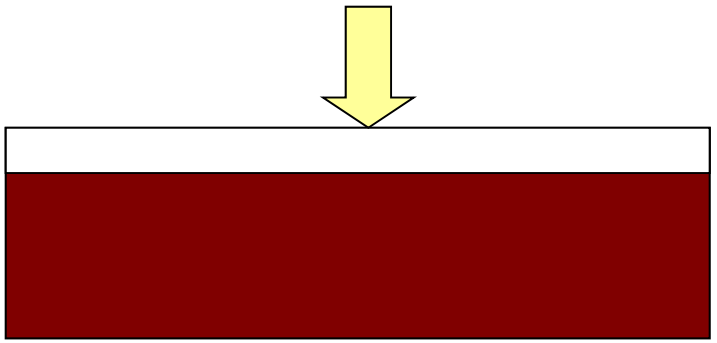
DiazoDiNitroPhenol

1. Low initiating ability, minimum load is as high as 120mg for RDX

2.Very serious waste water with deep color, pollution is very heavily

3. Mainly used in mining caps

Deep color waste water



Now 5 Mixing Compositions

Multiple salts： KD

Basic lead picrate, Lead azide, basic lead azide, lead nitrate formed in quantitatively, stable mixture

Co-precipitates： DS

Lead styphnate and lead azide formed co-precipitate chemically

Characteristics

1. All of them are high sensitive to mechanical percussion, stab, and friction stimulus！

2. Safety is the main concerns during the production and applications

3. Stability and compatibility is not as good as desired

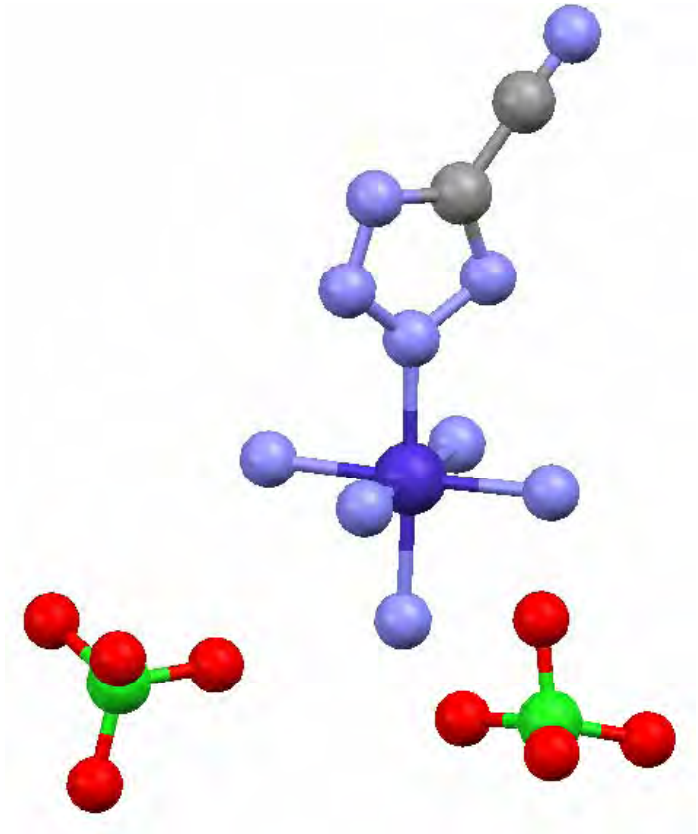
The development orientation for new primary explosive

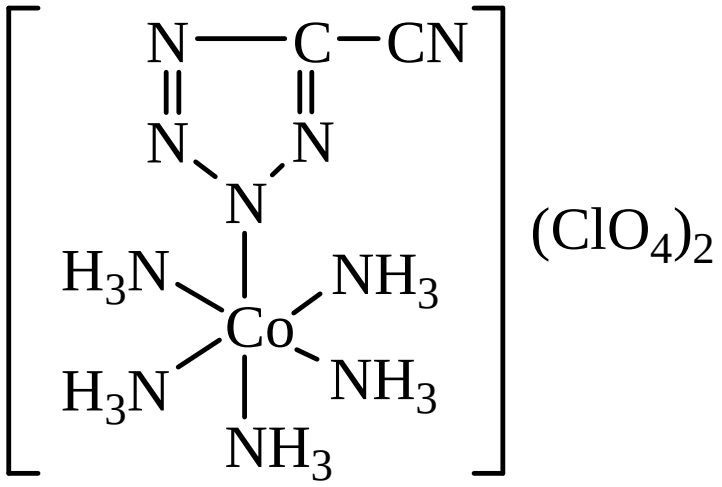
Coordination Compounds

$$[M\ Lx\ ](A)y$$

Cobalt 5-cyano-tetrazolato-quino amines Perchlorate

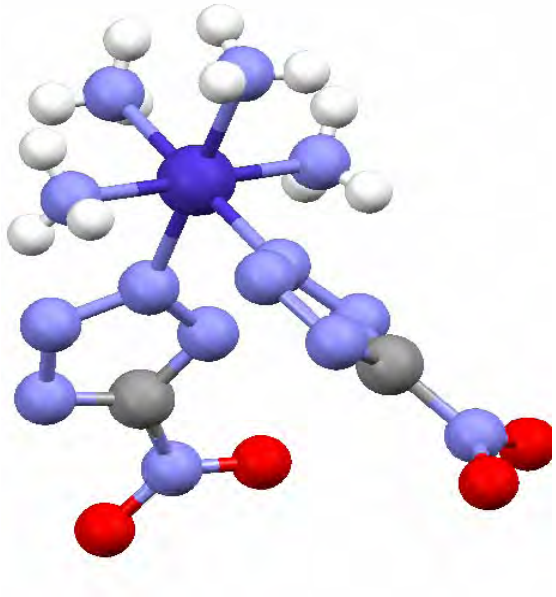
- **60’s，Sandia National lab. CP explosive**

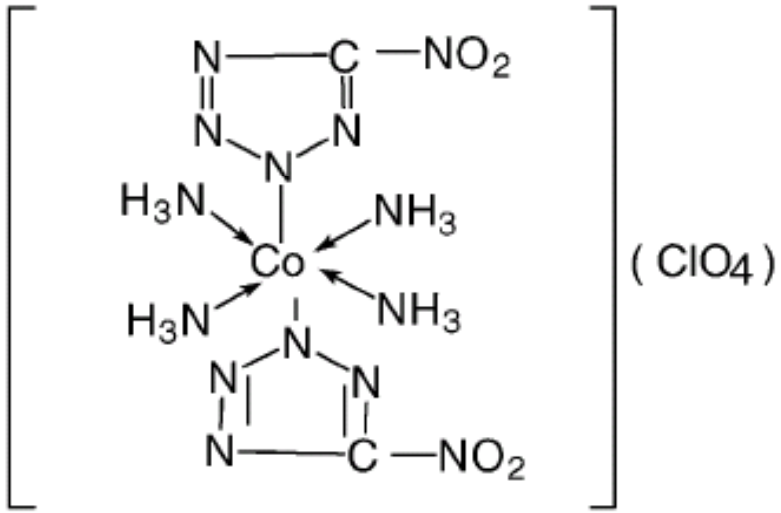




Cobalt bis(5-nitro-tetrazolato)-teraamines Perchlorate

- 1986，Bate declared BNCP explosive；
- 2005，Talawar reported BNCP, Ni、Cu and Zn from India





Drawbacks

- **Very time consuming for preparation**
- **Very low yield**
- **Very expensive**
- **Not suitable for large scale application**

Design of New Primary Explosive

In our group

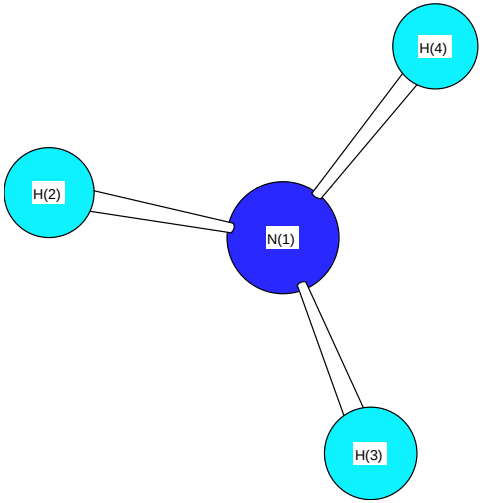
Selection of Metals

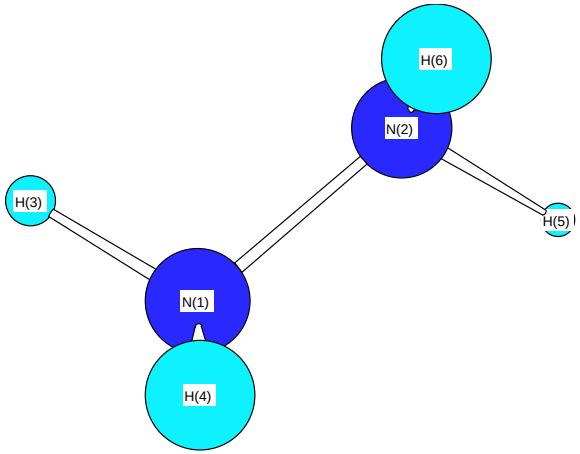
- ***s* IA ：K , Cs**
- ***s* IIA ： Mg, Ca , Sr, Ba**
- ***p heavy metal* ：Pb、 Bi**
- ***d* zone： Mn、Fe、Co、Ni**
- ***ds zone*：Cu、Zn、Cd、Ag、 Hg**
- **Main concerns are cost, toxicity and pollution**

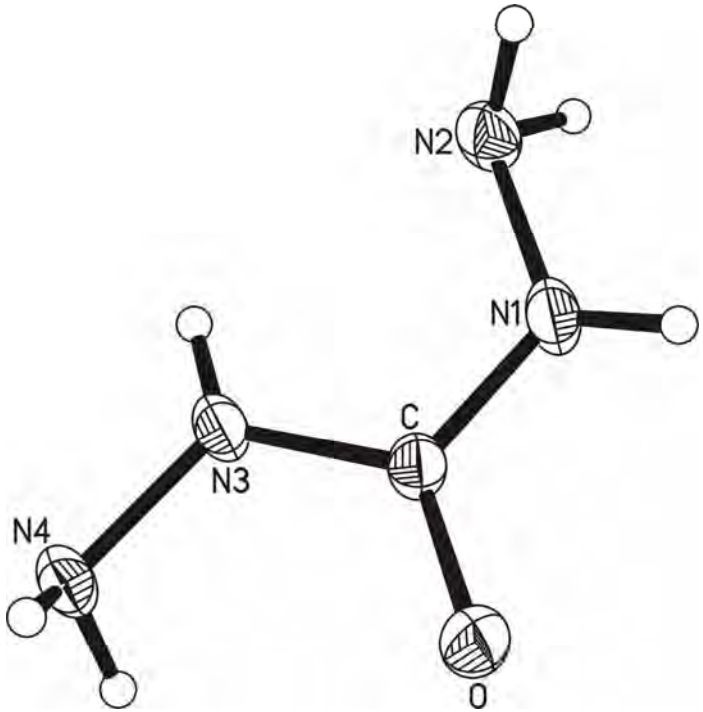
Selection of Ligand

1. **Amonia, hydrazine, carbohydrazine, amonourea、 aminoguandine, carbazate**
2. **TO、 NTO 、ATO、DATZ、ATZ et al nitrogen rich heterocycle compounds**

Ligand







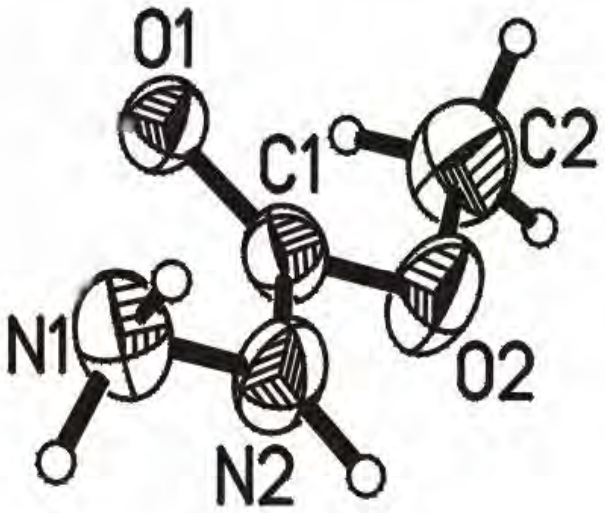
NH_3

NH_2NH_2

Carbohydrazide

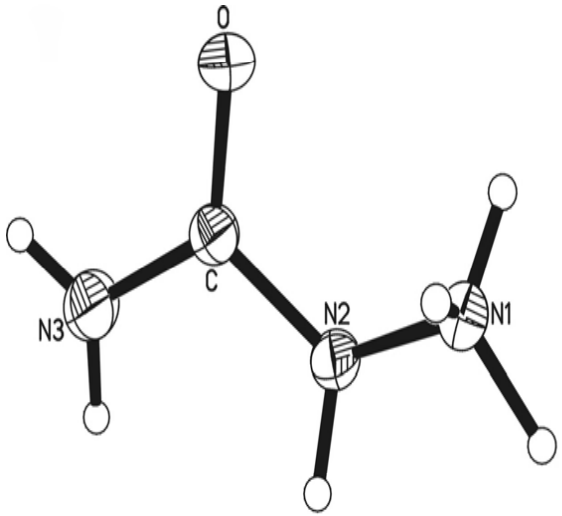
CHZ

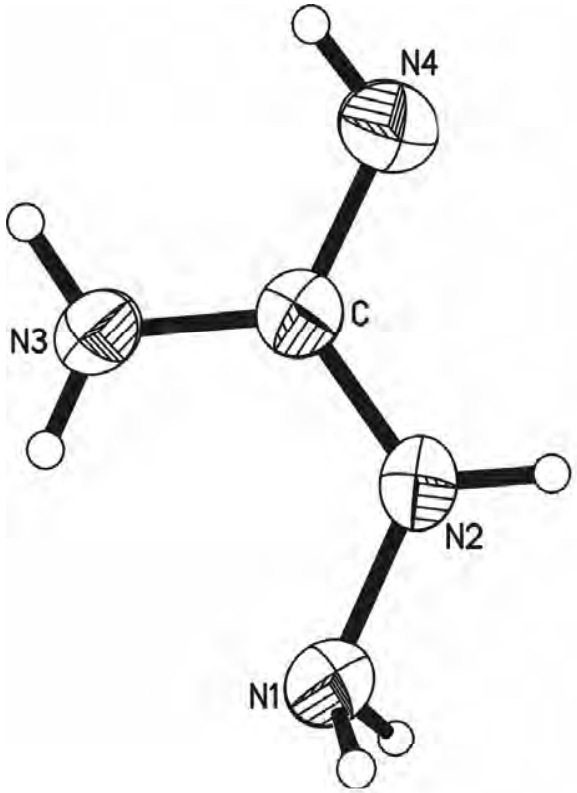
Ligand



MHC

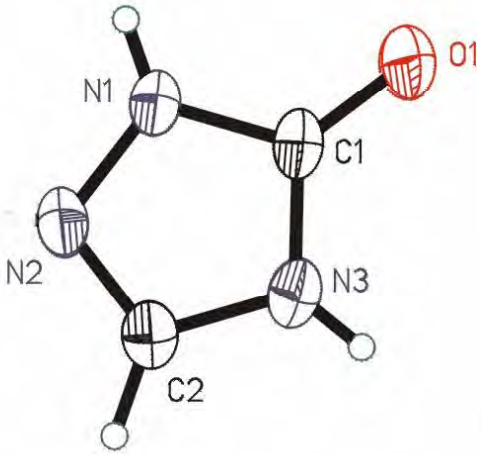
AU



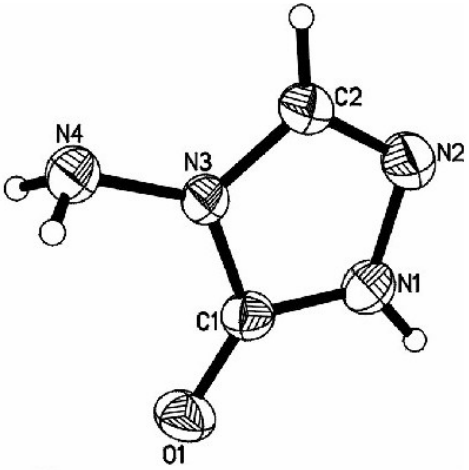


AG

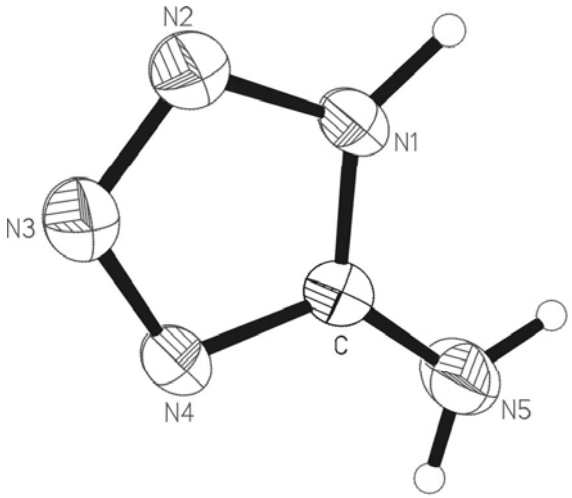
Ligand



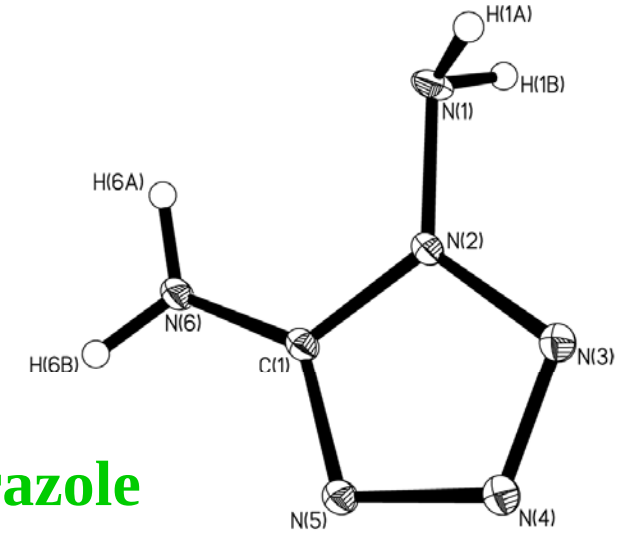
Triazone



AminoTriazone



AminoTetrazole



1,5-DiAminoTetrazole

Characteristics of ligands

- High nitrogen contents
- Give out high quantity of gas and energy
- Good stability in ordinary conditions

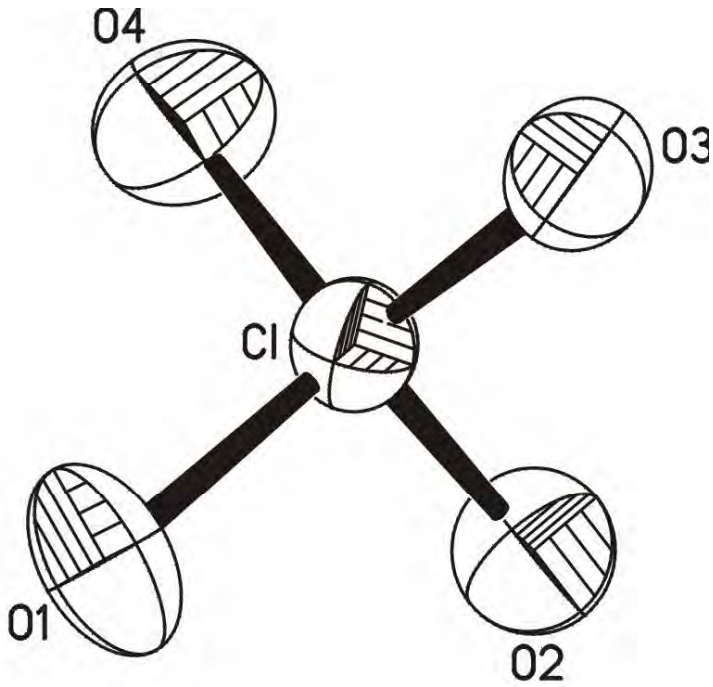
Selection of Anion

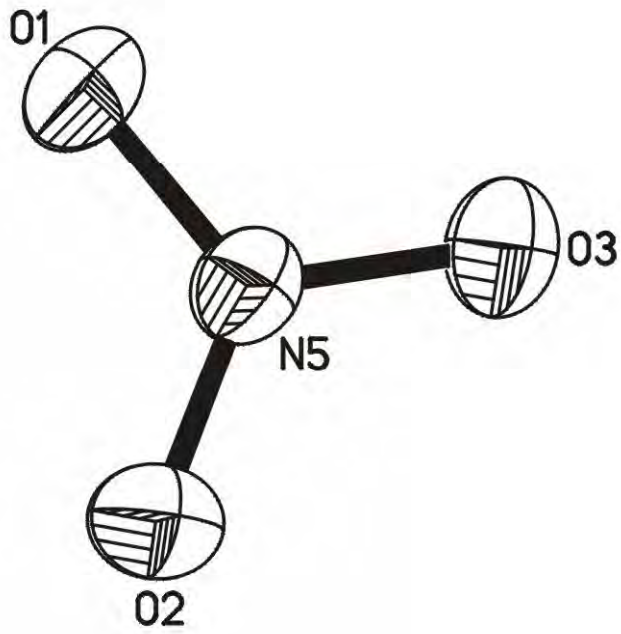
- **Oxygen deliver and high oxidization ability**
- **Easy explode or potential explosive**
- **Suitable stability, and easy be initiated to combustion or explode by external stimulus**

Anions

- **Inorganic：nitrate, perchlorate**
- **Organic：DAN、trinitromethane、picrate, styphnate, NTO et al.**

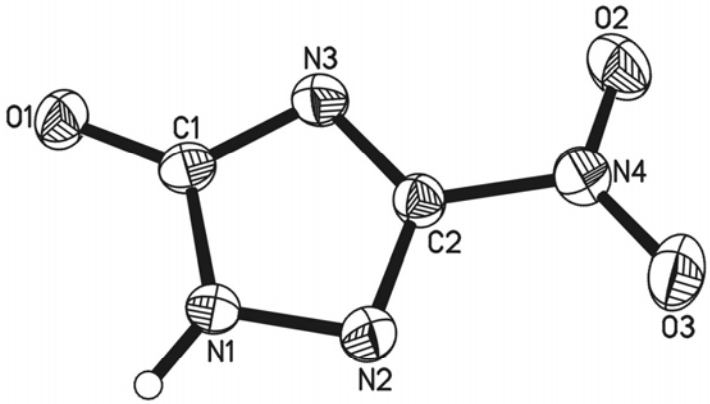
Structures of Anions



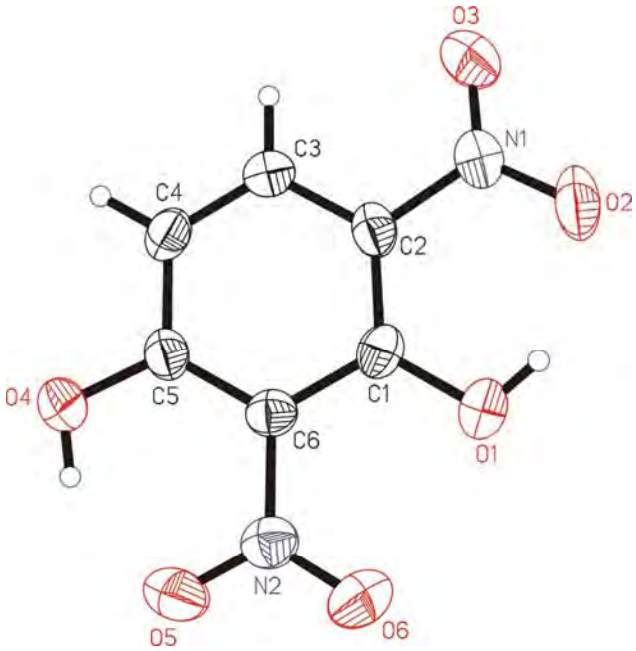


ClO_4^- NO_3^-

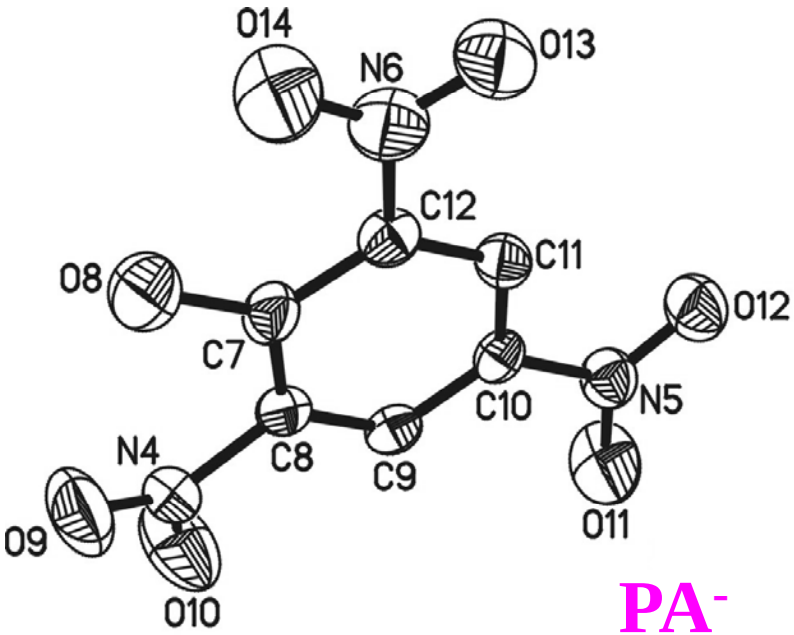
Structures of Anions



NTO^-



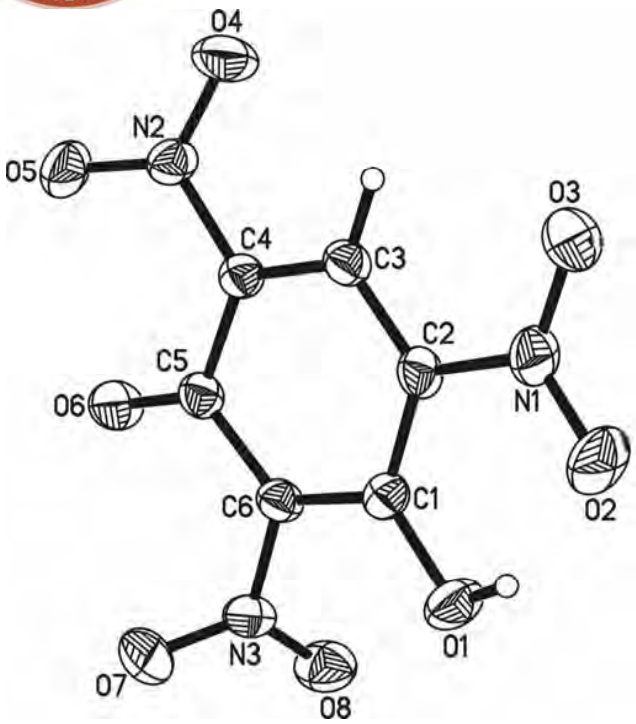
DNR



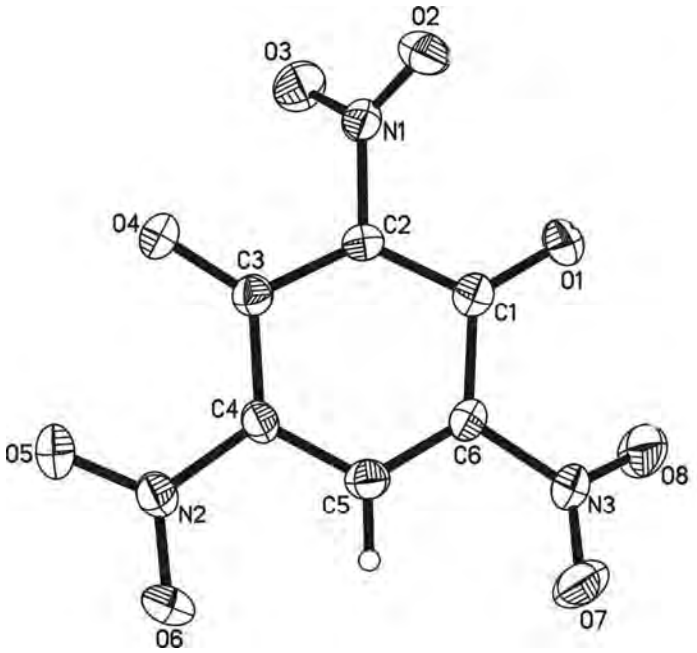
PA^-

Structures of Anions

Styphnates

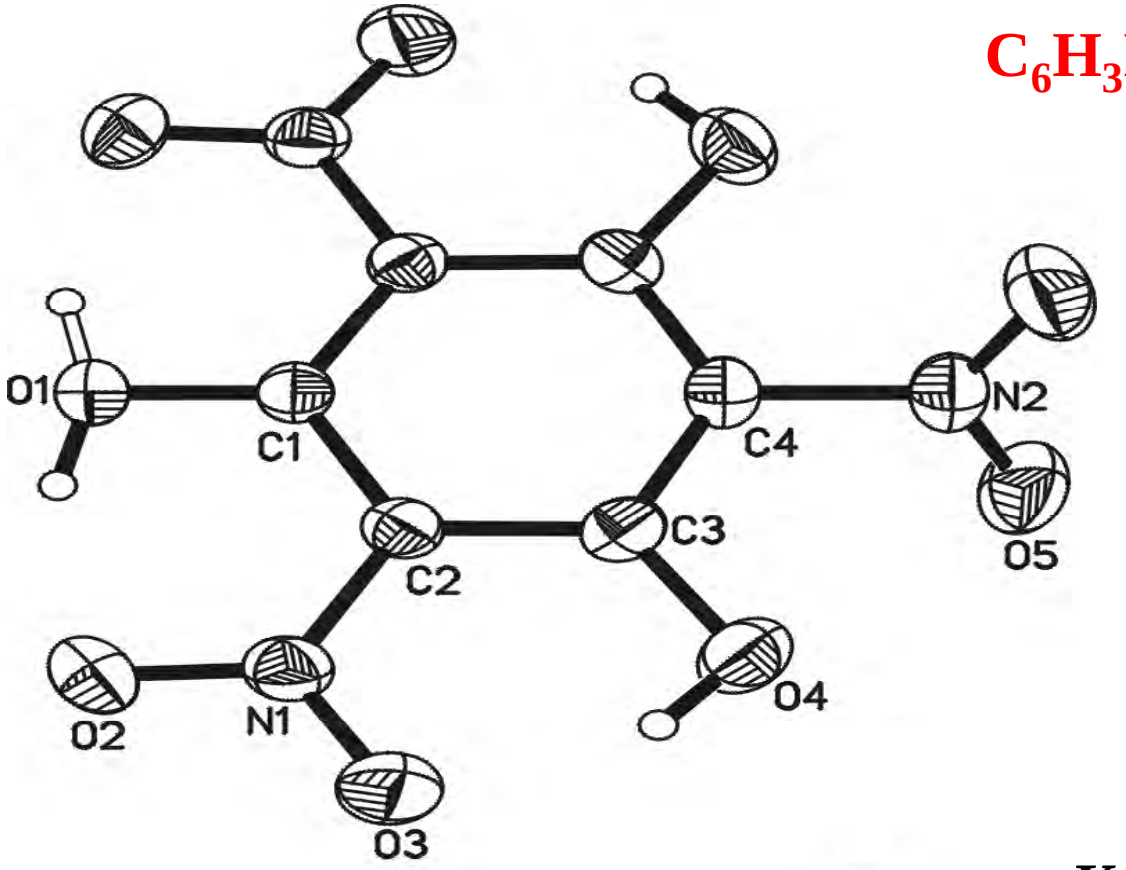


$HTNR^-$



$TNR^=$

Structures of Anions



$C_6H_3N_3O_9 \cdot 2/3H_2O$

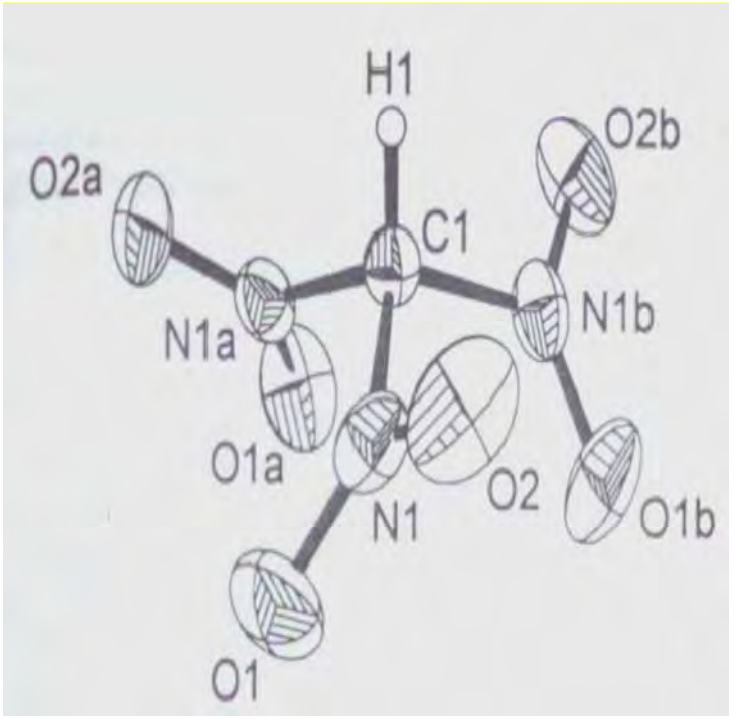
TNPG

$K_1 \approx 1.52 \times 10^{-2}$

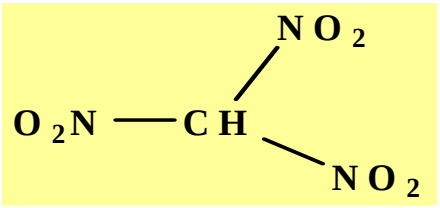
$K_2 \approx 2.44 \times 10^{-4}$

$K_3 \approx 6.3 \times 10^{-8}$

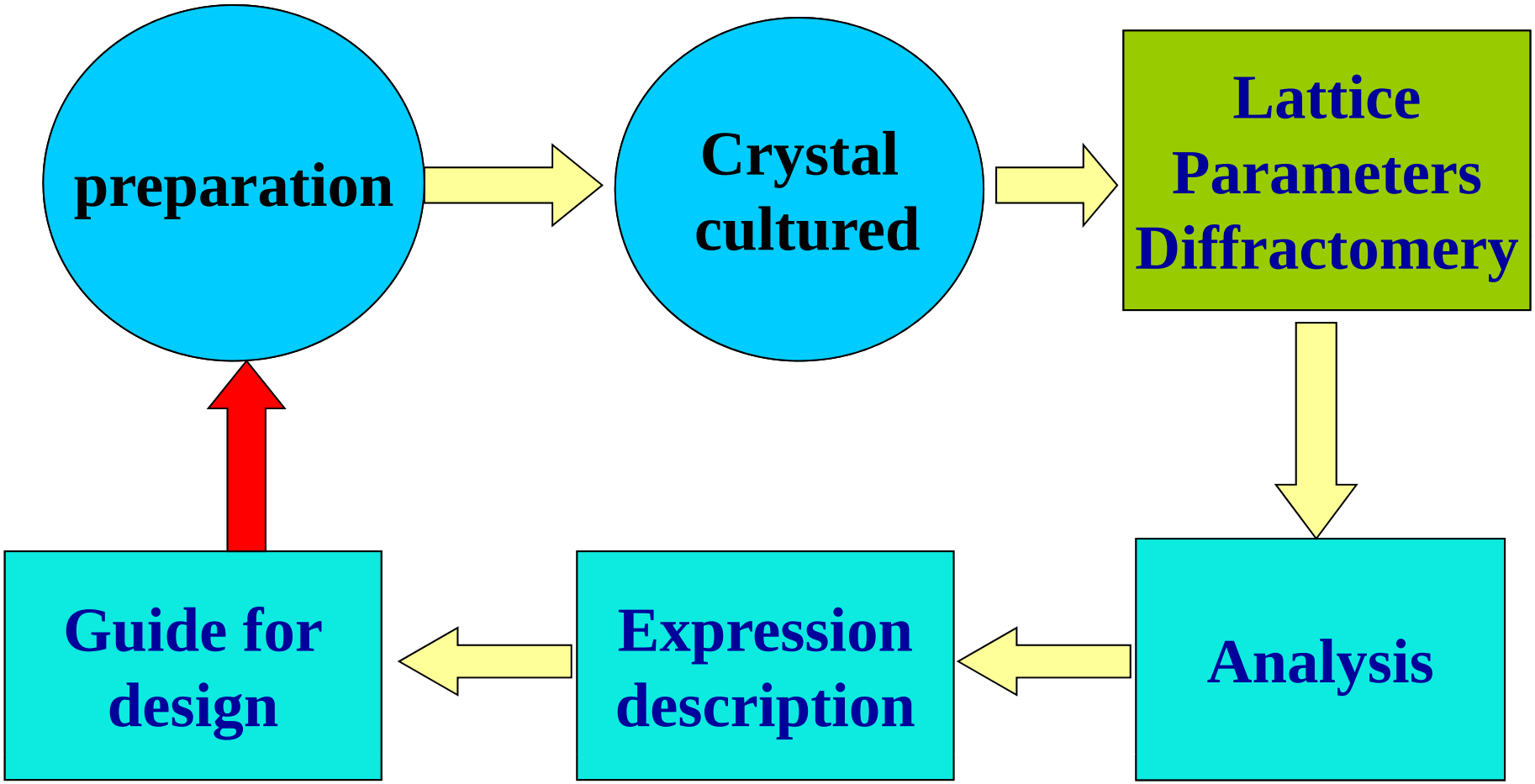
Structures of Anions



Trinitromethane



X-ray methods



Diffractometer

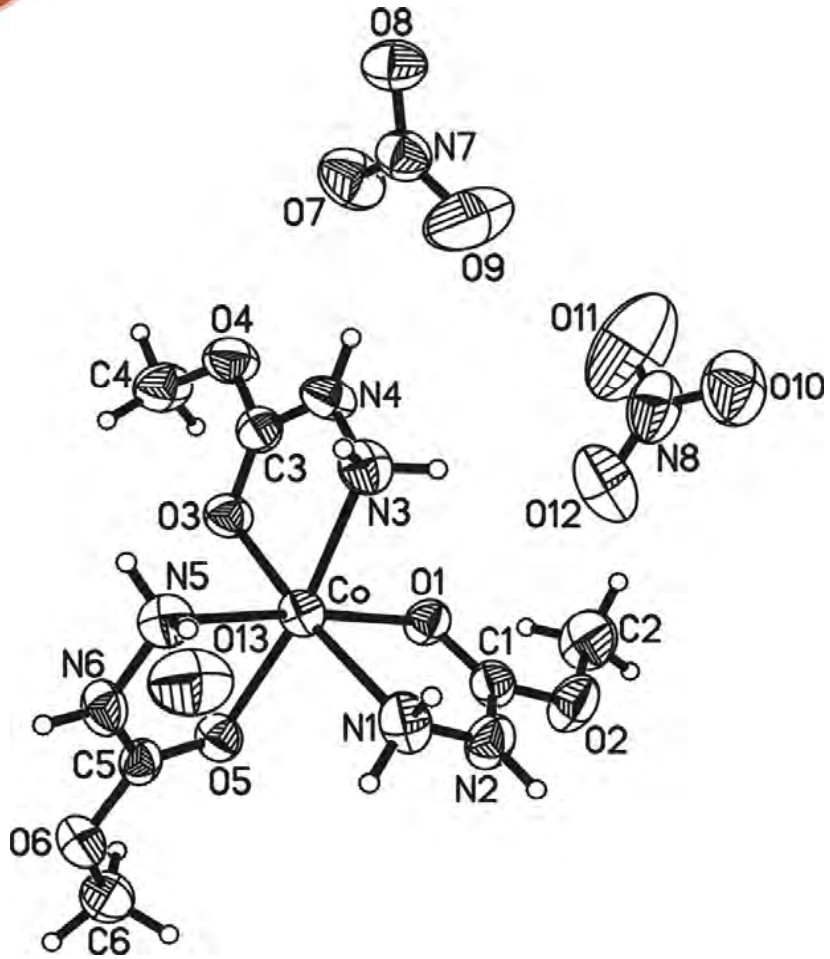
- **Rigaku X-ray diffractometer**
- **Saturn 724$^+$ CCD**
- **MoK_α, -180 ℃**
- **Graphite monochrome**
- **λ=0.071073 nm**

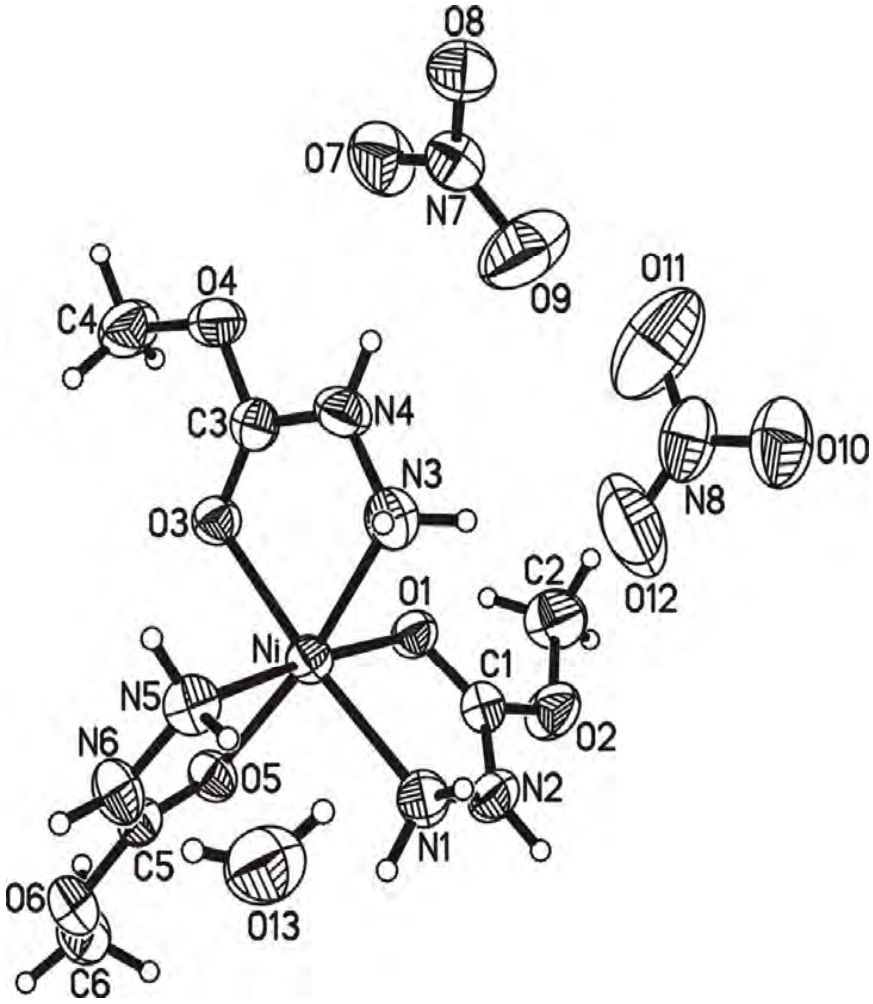
Diffractometer

New Synthsized Compounds

1. Nitrates
2. NTO
3. Picrates
4. Styphnates
5. TNPG
6. Trinitromethanes
7. Perchlorate

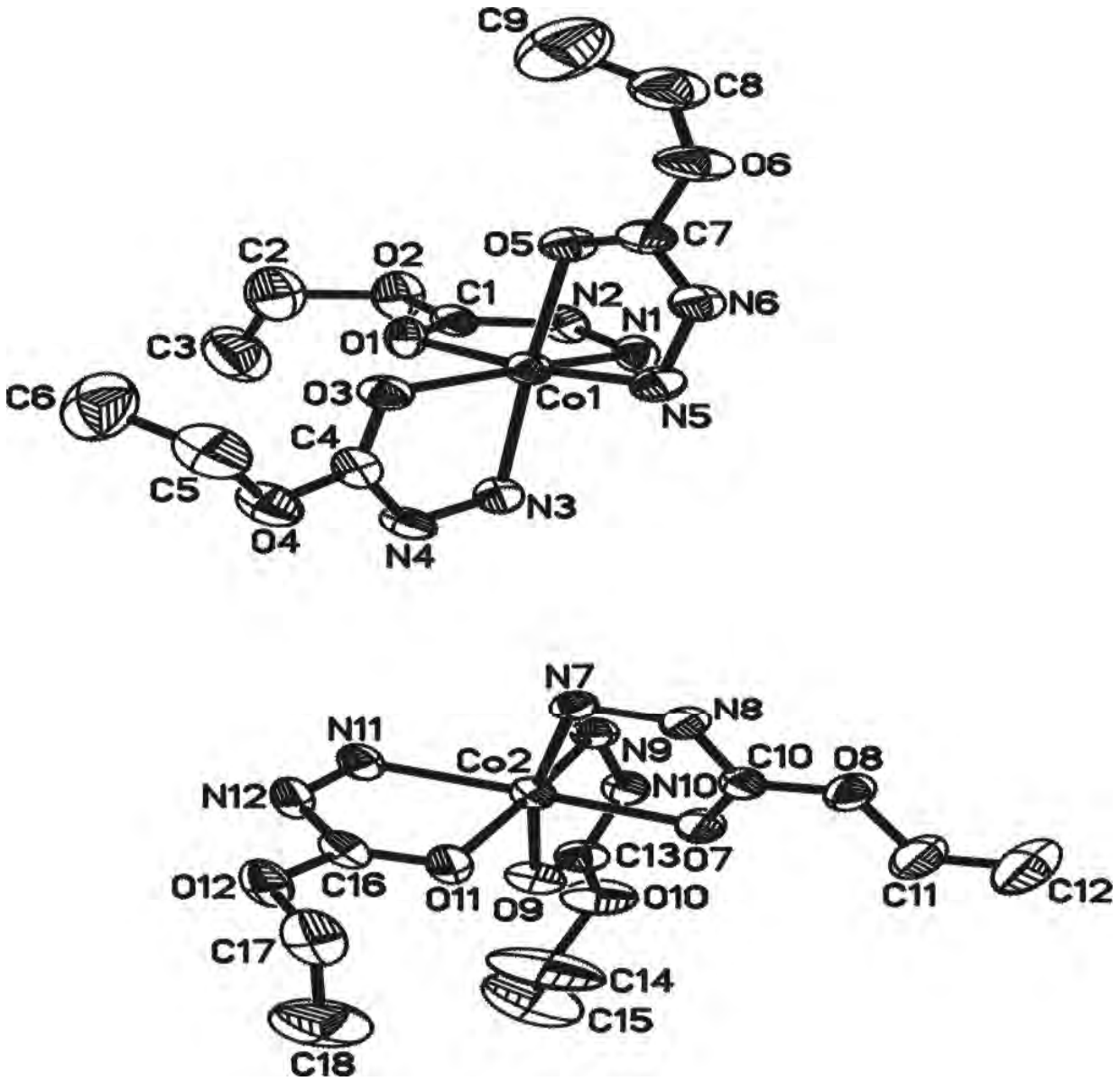
Nitrates



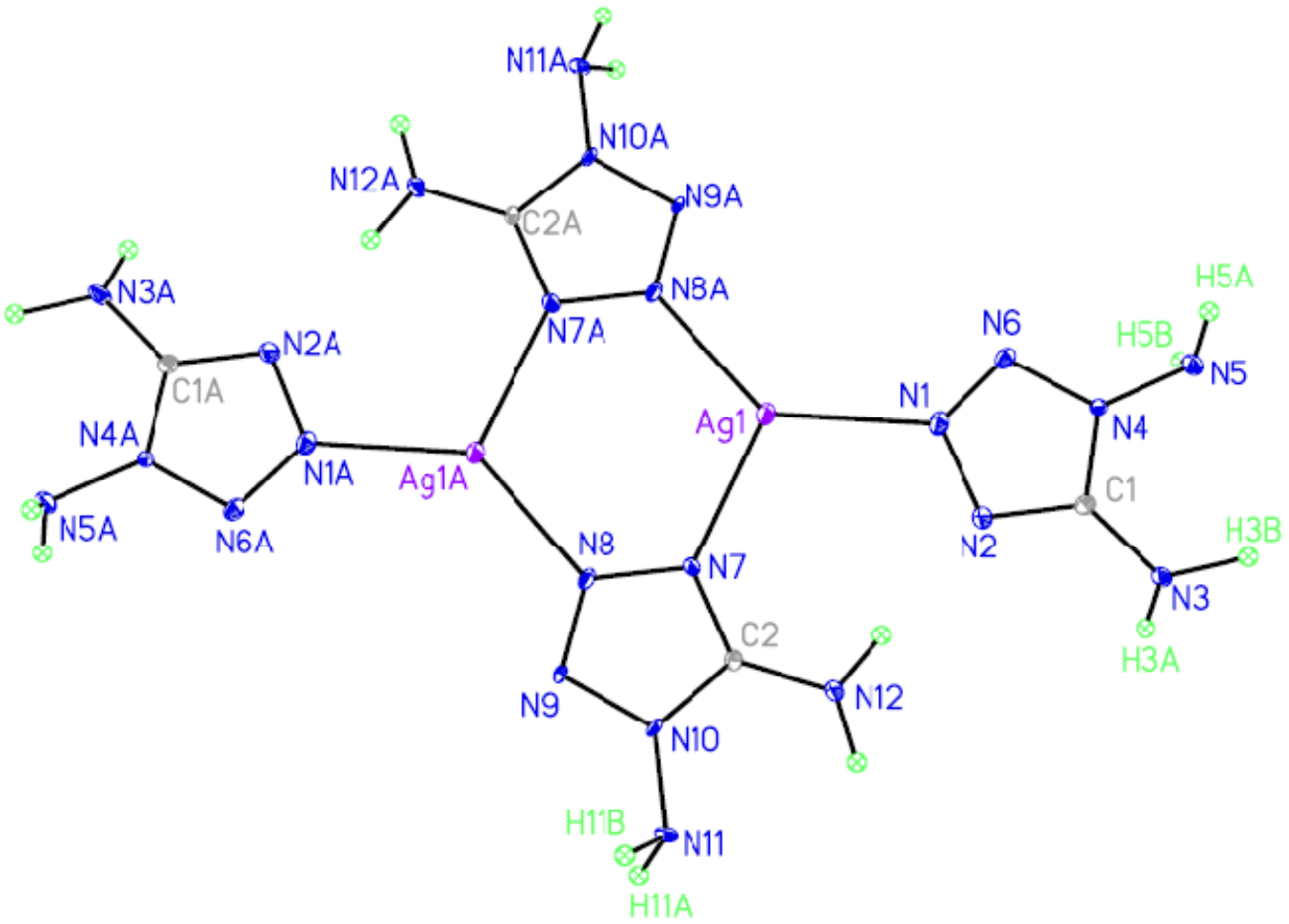


$[Co(MHC)_3](NO_3)_2 \cdot H_2O$

$[Ni(MHC)_3](NO_3)_2 \cdot H_2O$



$\{[Co(EHC)_3](NO_3)_2\}_2$



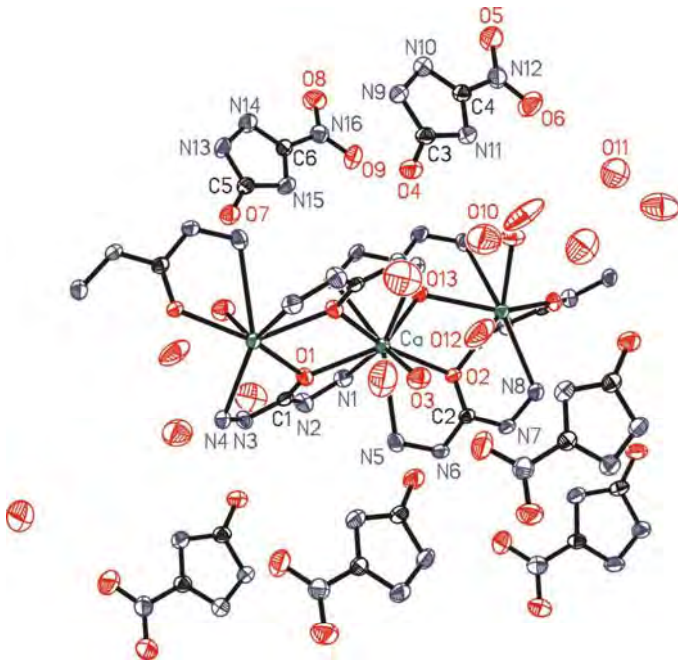
$[Ag_2(DAT)_4](NO_3)_2$

Findings

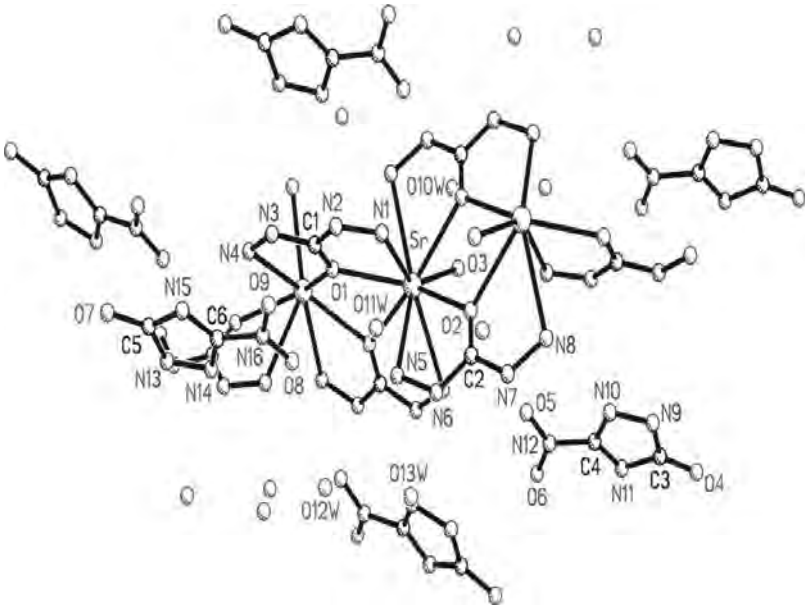
- **Easy dissolved in solvents, hard to culture single crystal**
- **Low oxidization ability, low explosive power $[Ni(NH_2NH_2)(NO_3)_2]_n$ is used in mining caps**

NTO

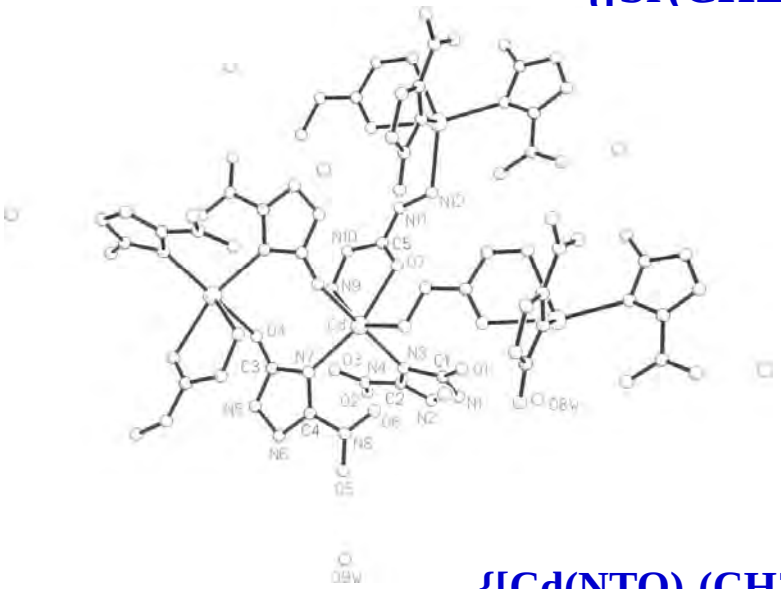
Compounds



$\{[Ca(CHZ)_2(H_2O)](NTO)_2 \cdot 3.5H_2O\}_n$



$\{[Sr(CHZ)_2(H_2O)](NTO)_2 \cdot 3.5H_2O\}_n$



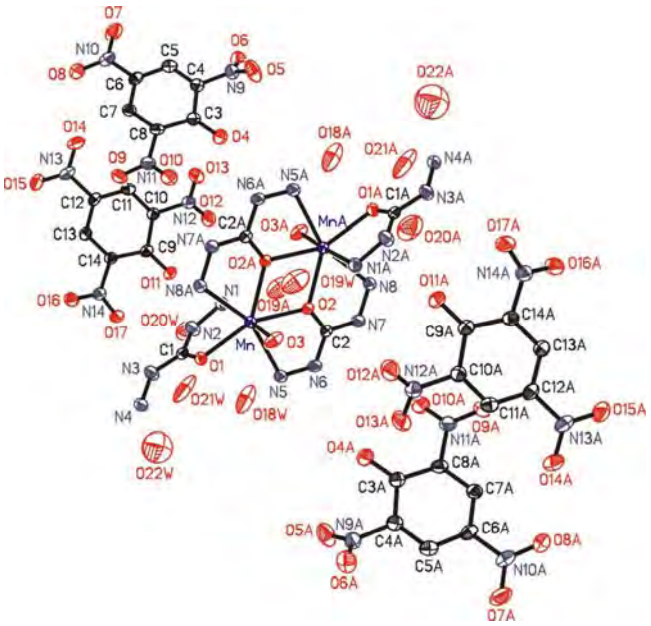
$\{[Cd(NTO)_2(CHZ)] \cdot 2H_2O\}_n$

NTO Findings

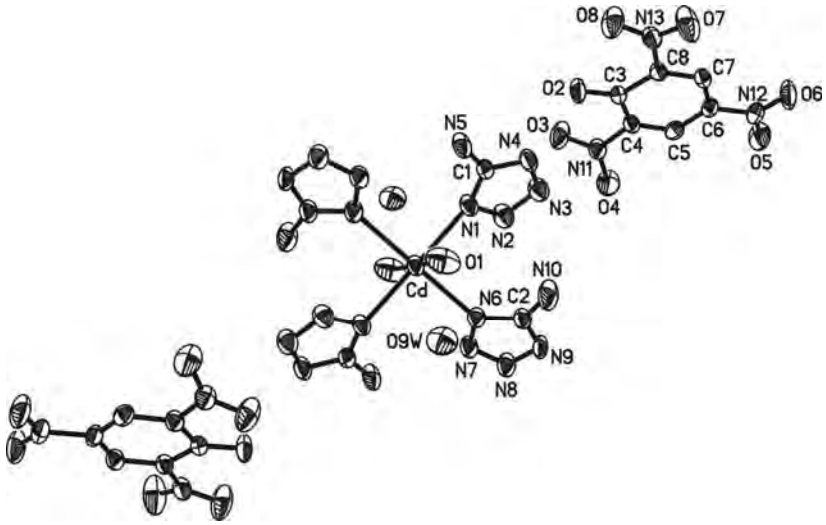
- NTO contained coordination compounds are easily to form 3D net structure
- Stable 5-ring exists for support the compounds
- NTO served as ligand or anion in these compounds
- Usually contain many coordination water and lattice waters

Picrate

Compounds



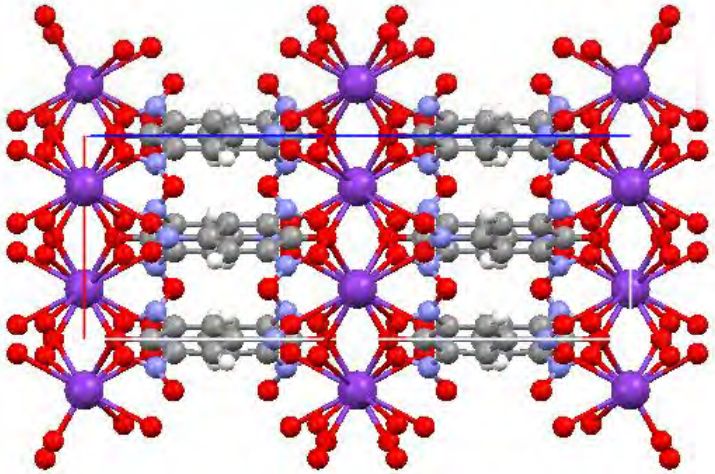
$[Mn_2(CHZ)_4(H_2O)_2](PA)_4 \cdot 10H_2O$

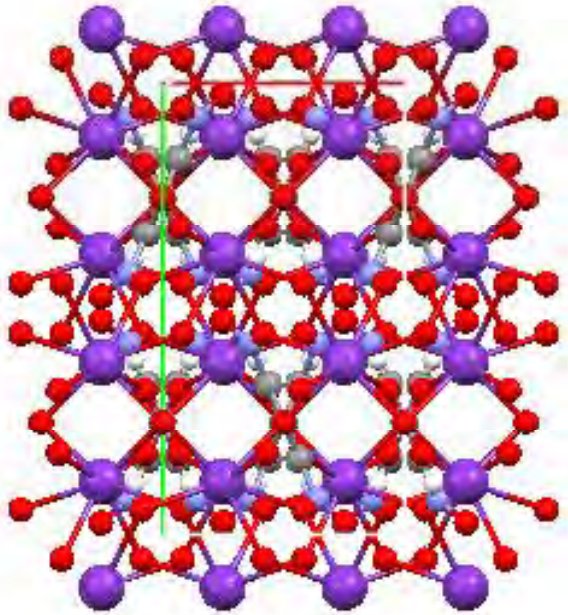


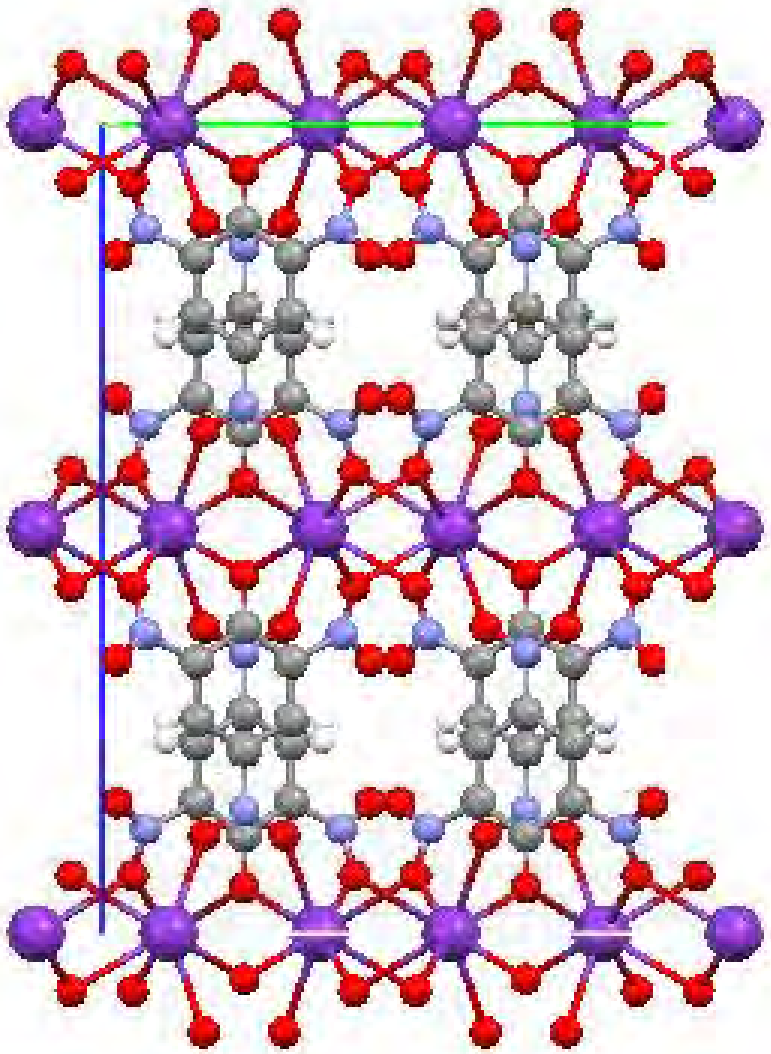
$[Cd(ATZ)_4(H_2O)_2](PA)_2 \cdot 2H_2O$

$[Mn(ATO)_2(H_2O)_4](PA)_2$

Potassium Picrate





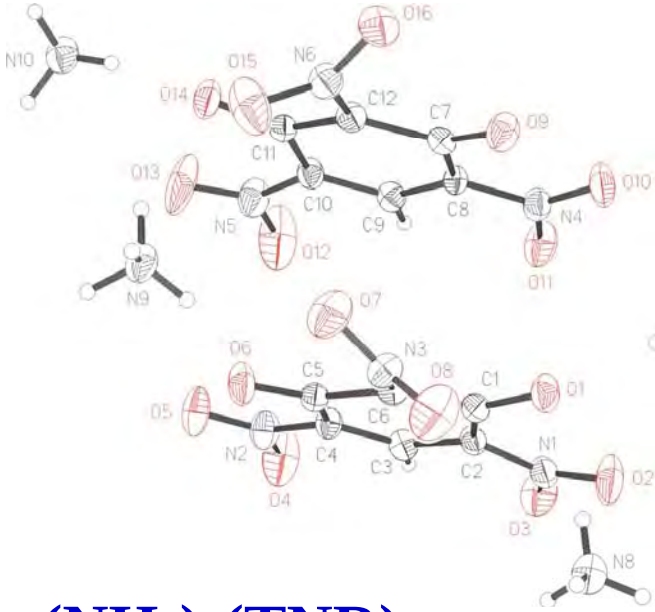


Findings for Picrates

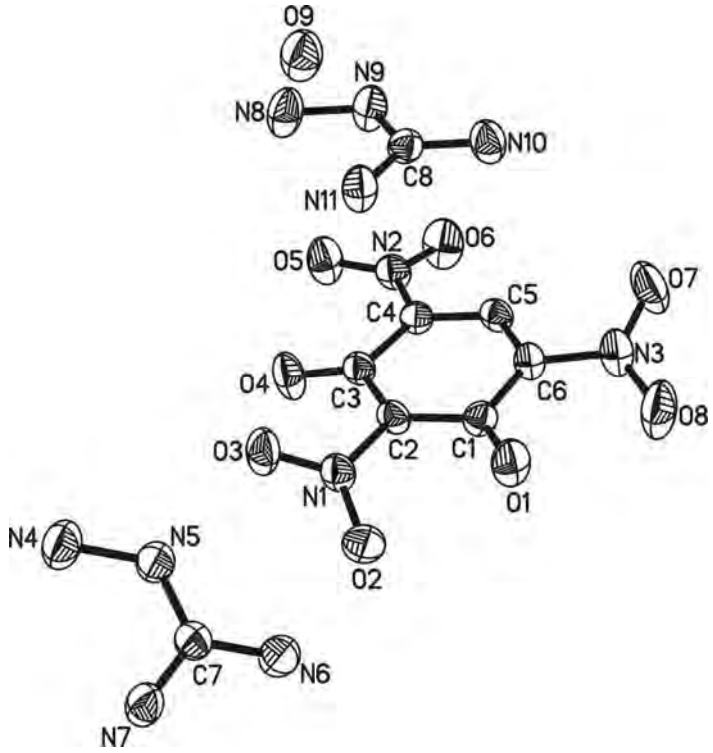
- **Picrate served as ligand and anion**
- **Some of the coordination compounds have coordination water or lattice waters**
- **Some of these compound used as ignition composition**

Styphnate

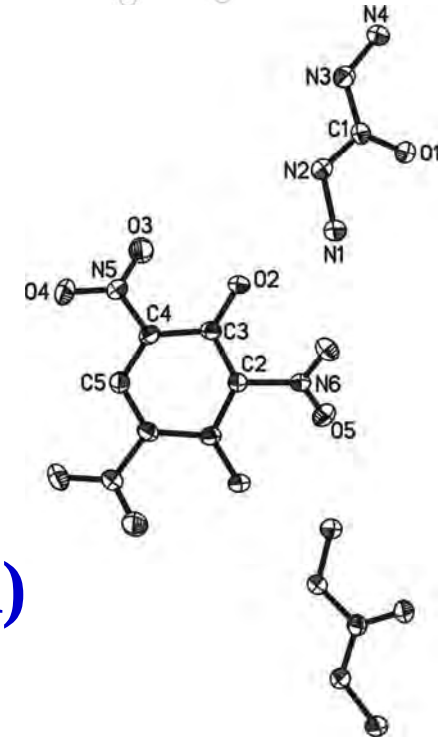
Compounds



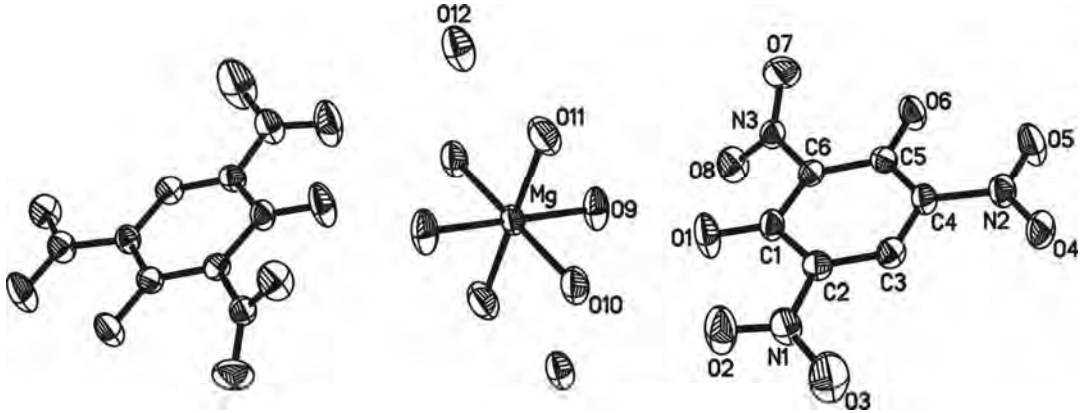
$(NH_4)_2(TNR)$



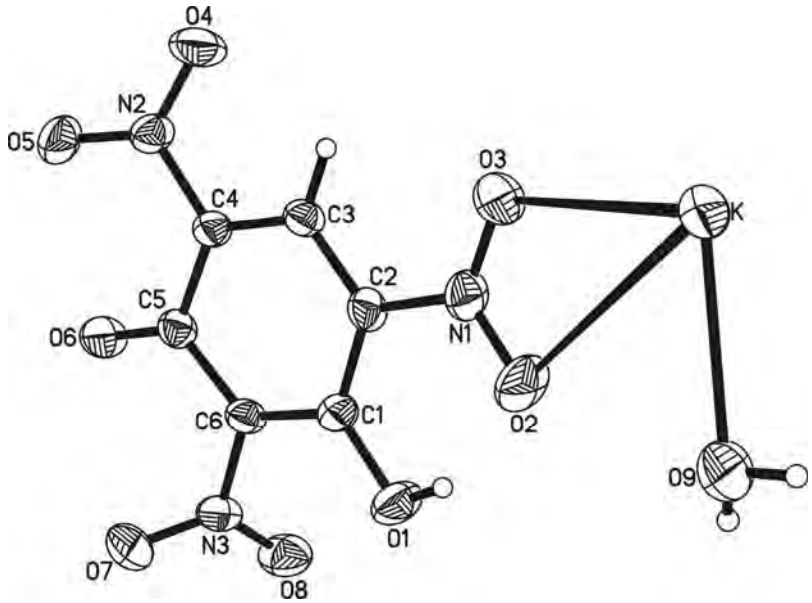
$(AG)_2(TNR)\cdot H_2O$



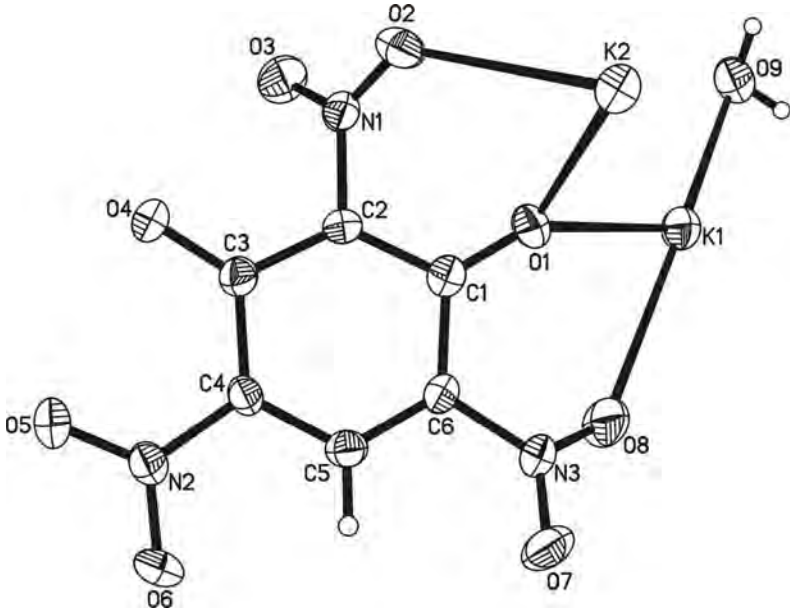
$(CHZ)_2(TNR)$



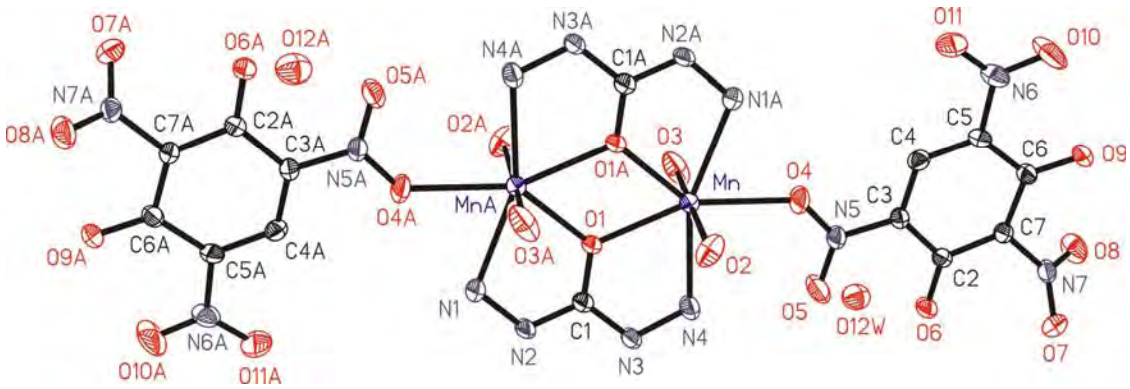
$[Mg(H_2O)_6](HTNR)_2 \cdot 2H_2O$



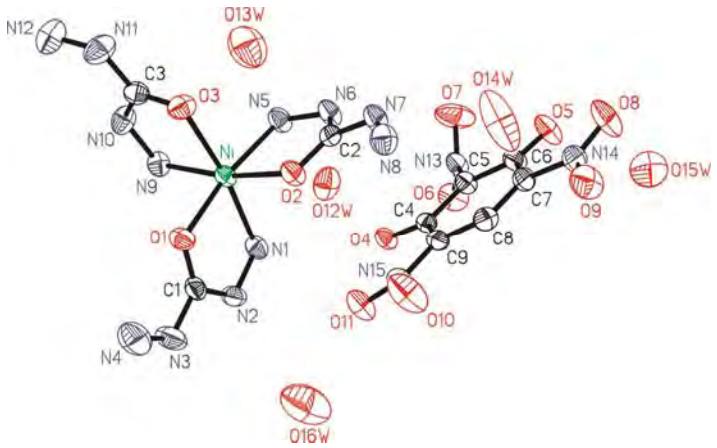
$[K(HTNR)\ (H_2O)]_n$



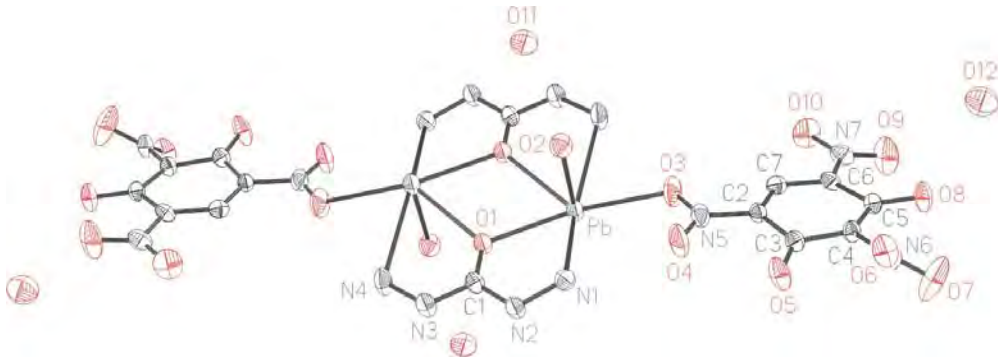
$[K_2(TNR)\ (H_2O)]_n$



$[Mn_2(TNR)_2(CHZ)_2(H_2O)_4]\cdot 2H_2O$

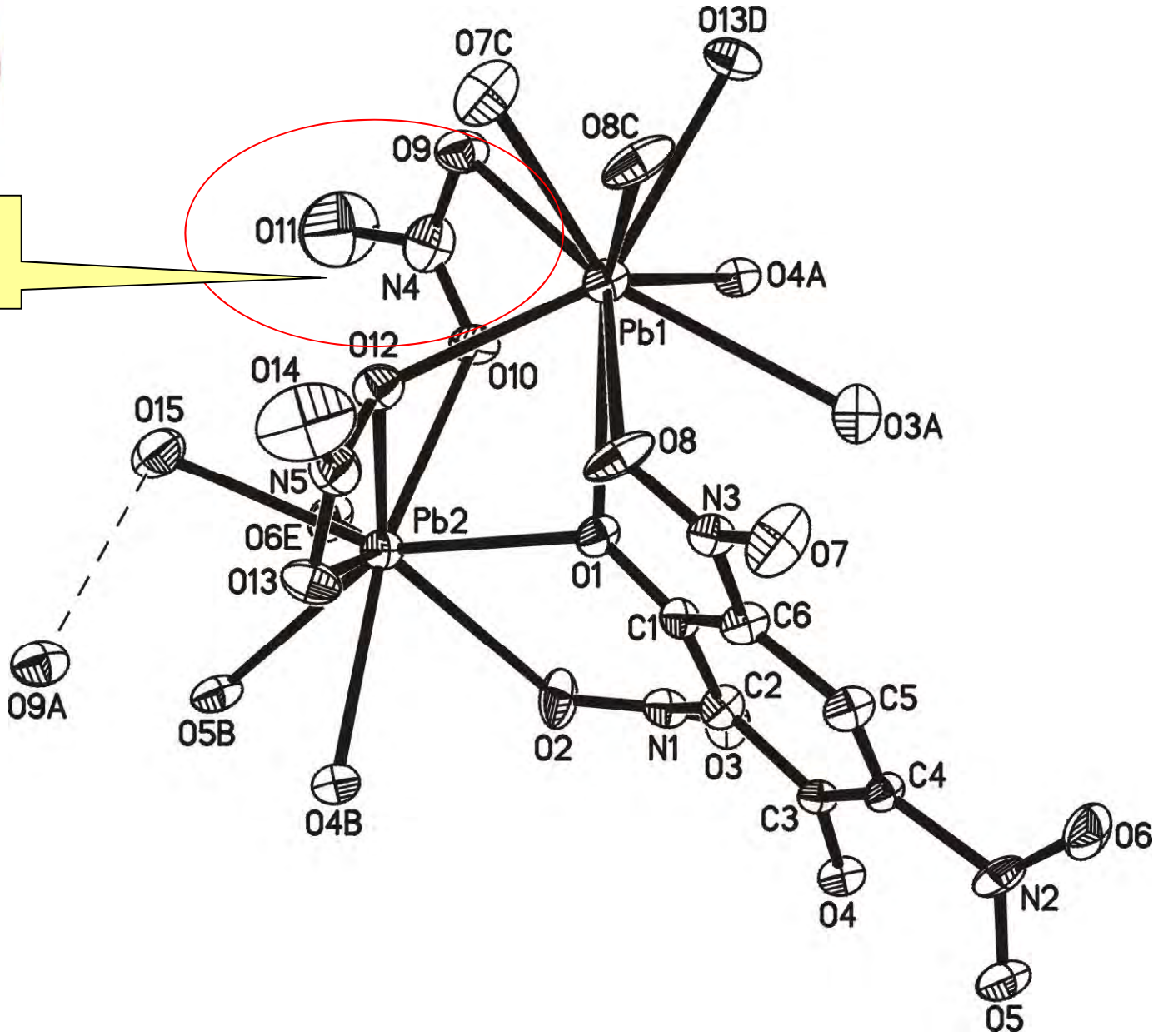


$[Ni(CHZ)_3](TNR)\cdot 5H_2O$



$[Pb_2(TNR)_2(CHZ)_2(H_2O)_2]\cdot 4H_2O$

NO_3^-



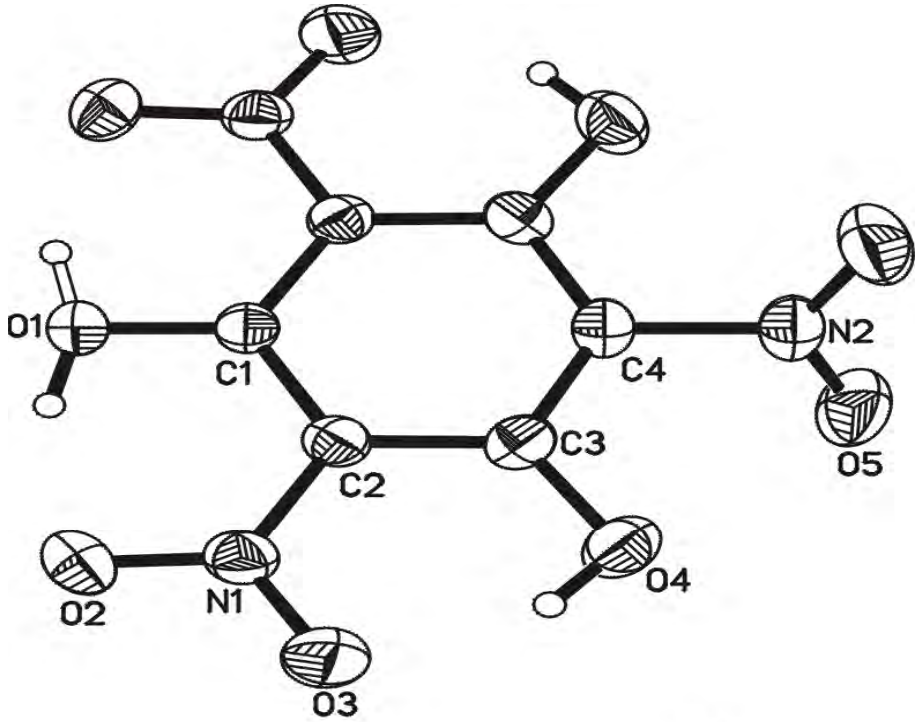
$[Pb_2(TNR)(NO_3)_2(H_2O)]_n$

TNPG

TriNitroPhloroGlucinol

Compounds

Properties

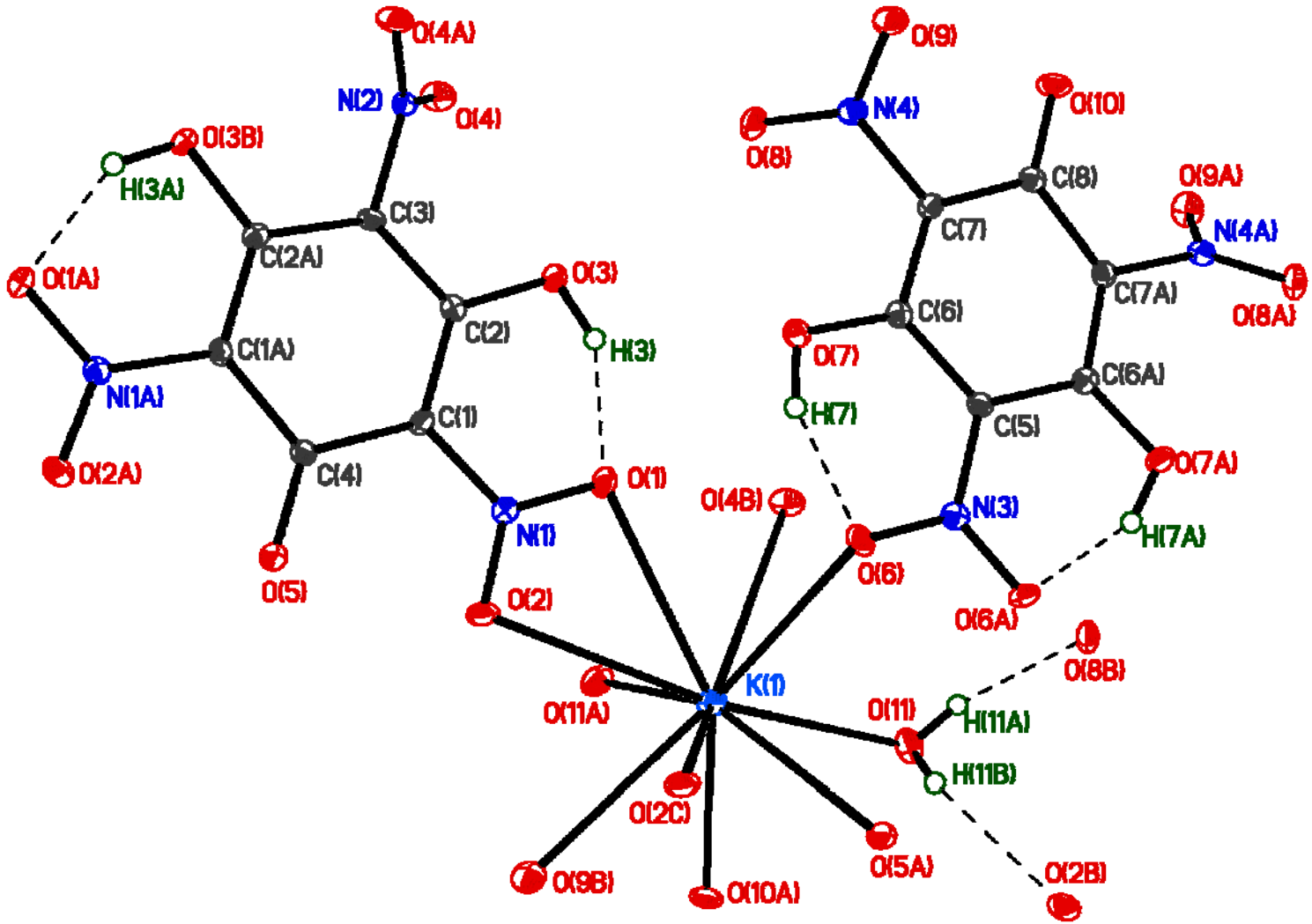


$K_1 \approx 1.52 \times 10\text{-}2$

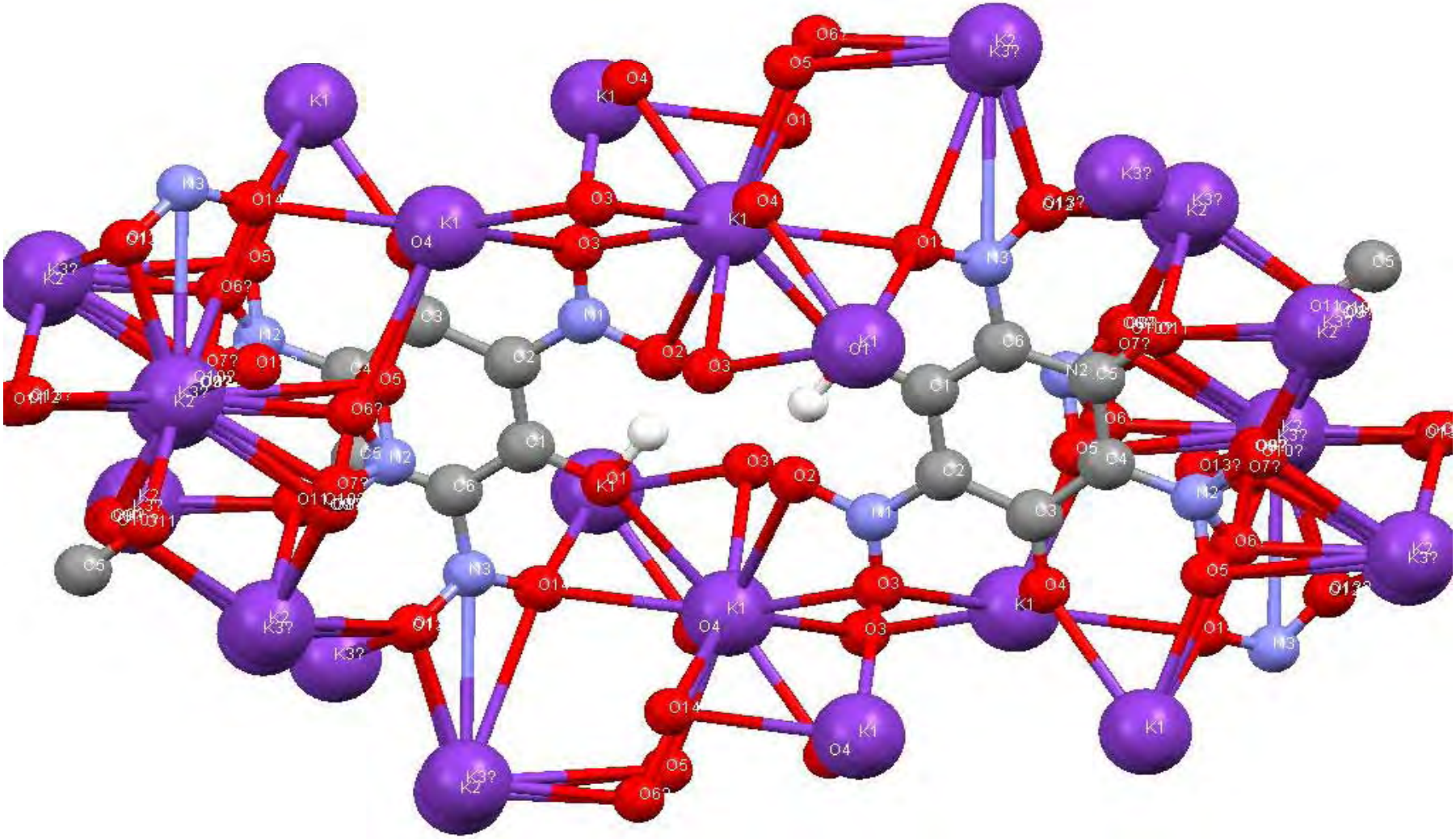
$K_2 \approx 2.44 \times 10\text{-}4$

$K_3 \approx 6.3 \times 10\text{-}8$

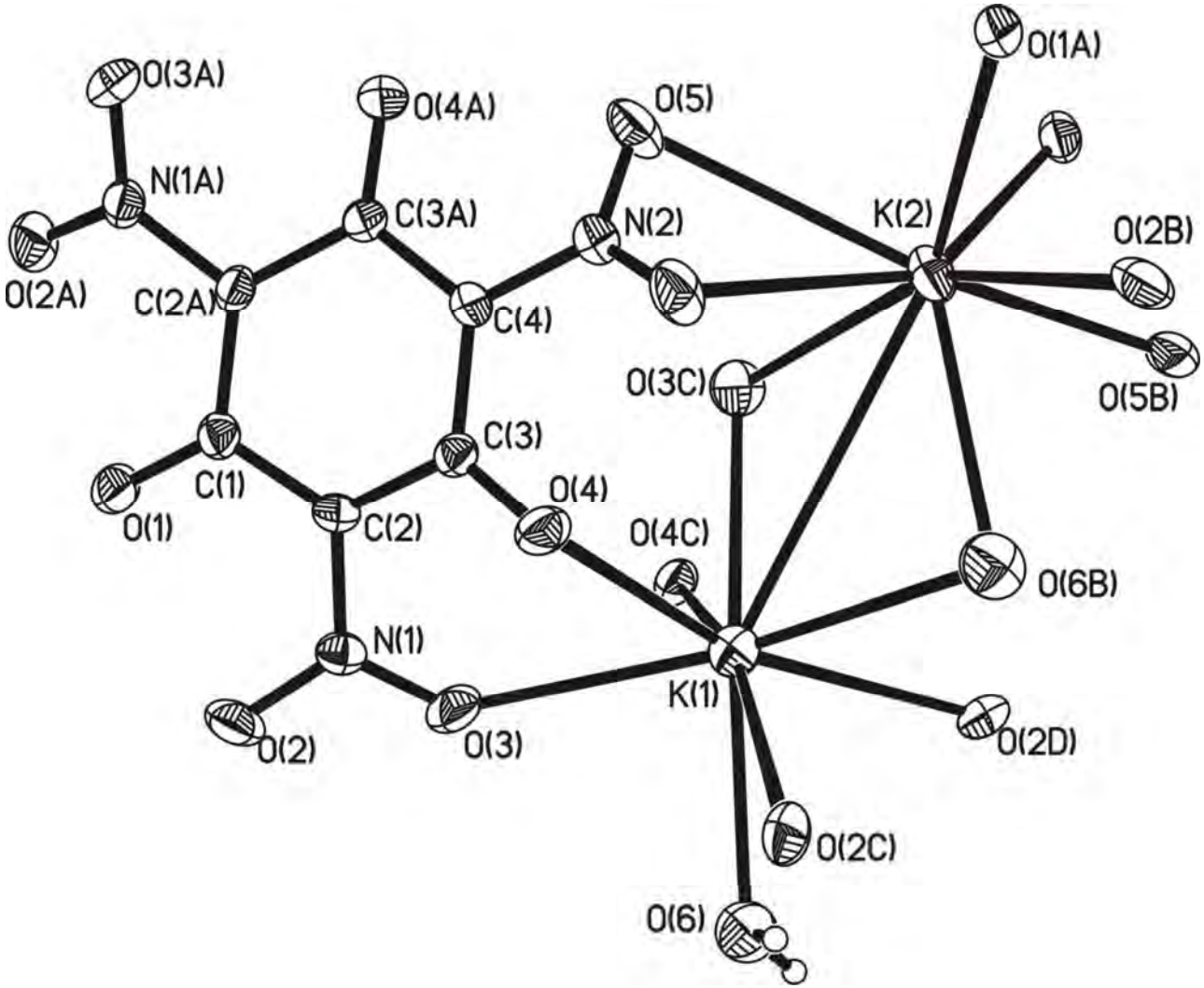
$[K(H_2TNPG)(H_2O)]_n$



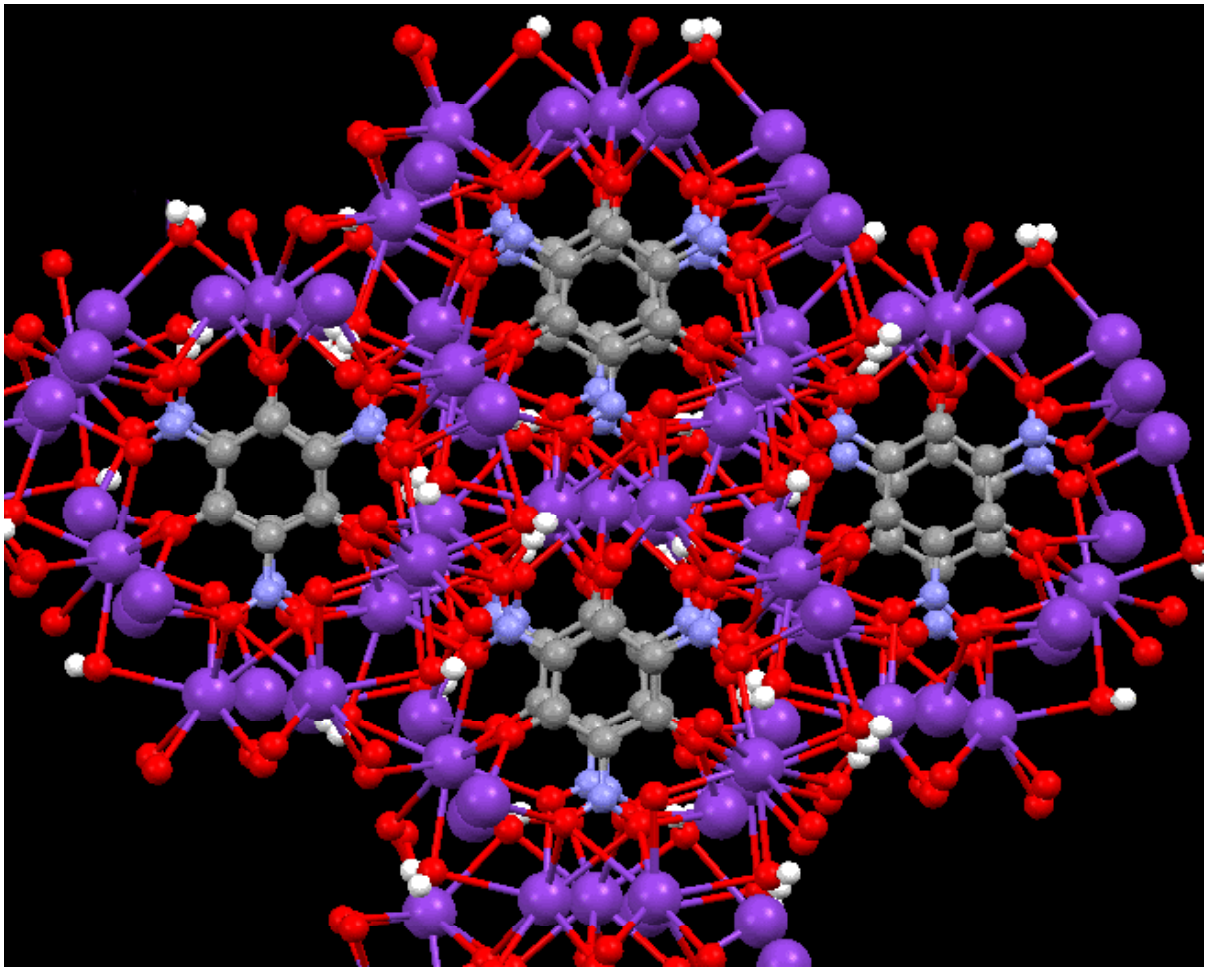
$[K_2(HTNPG)]_n$

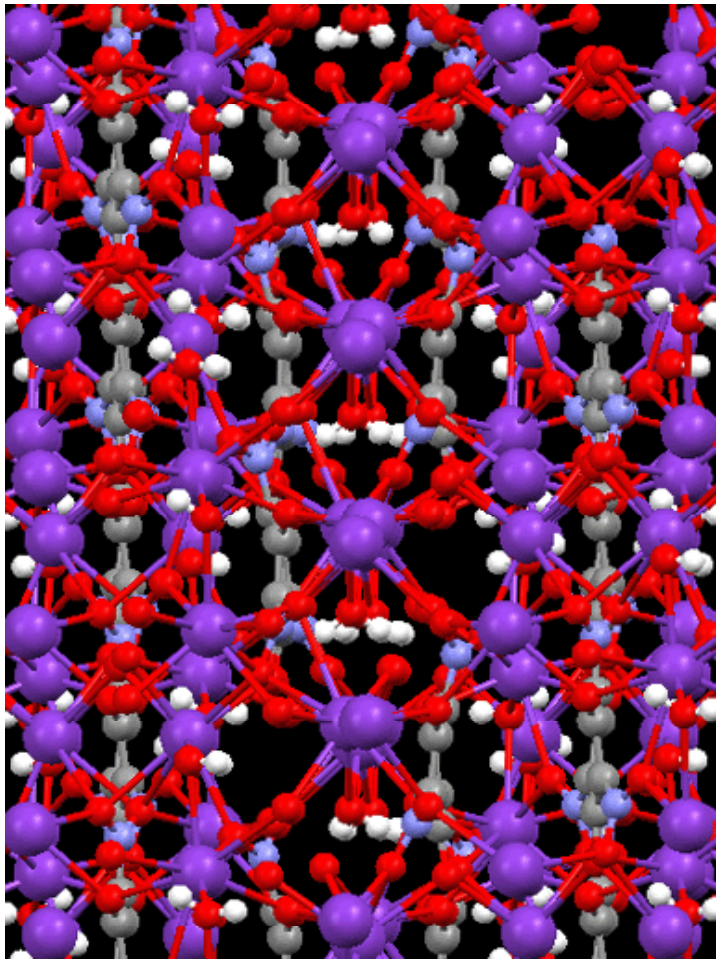


$[K_3(TNPG)(H_2O)_2]_n$

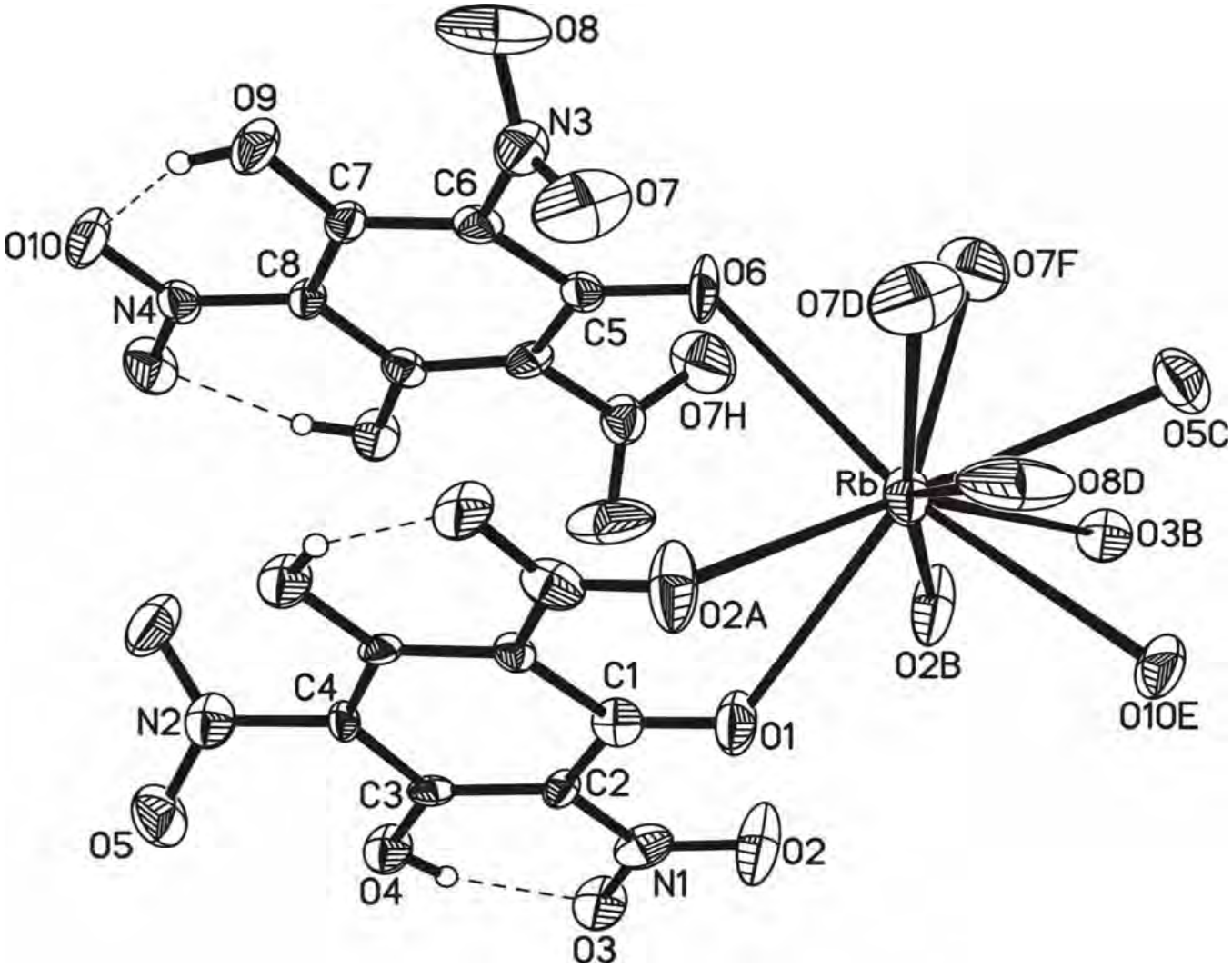


$[K_3(TNPG)(H_2O)_2]_n$

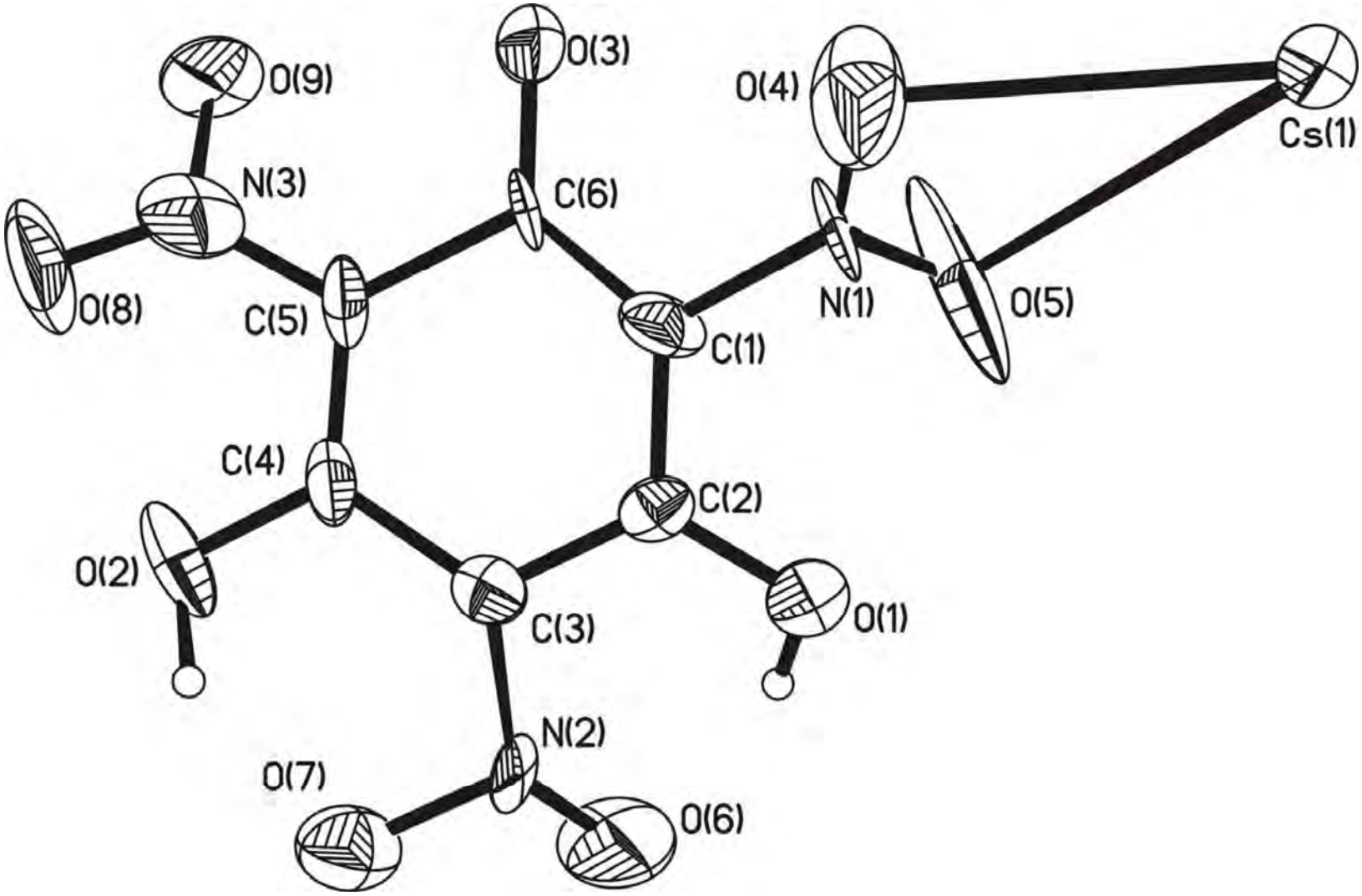




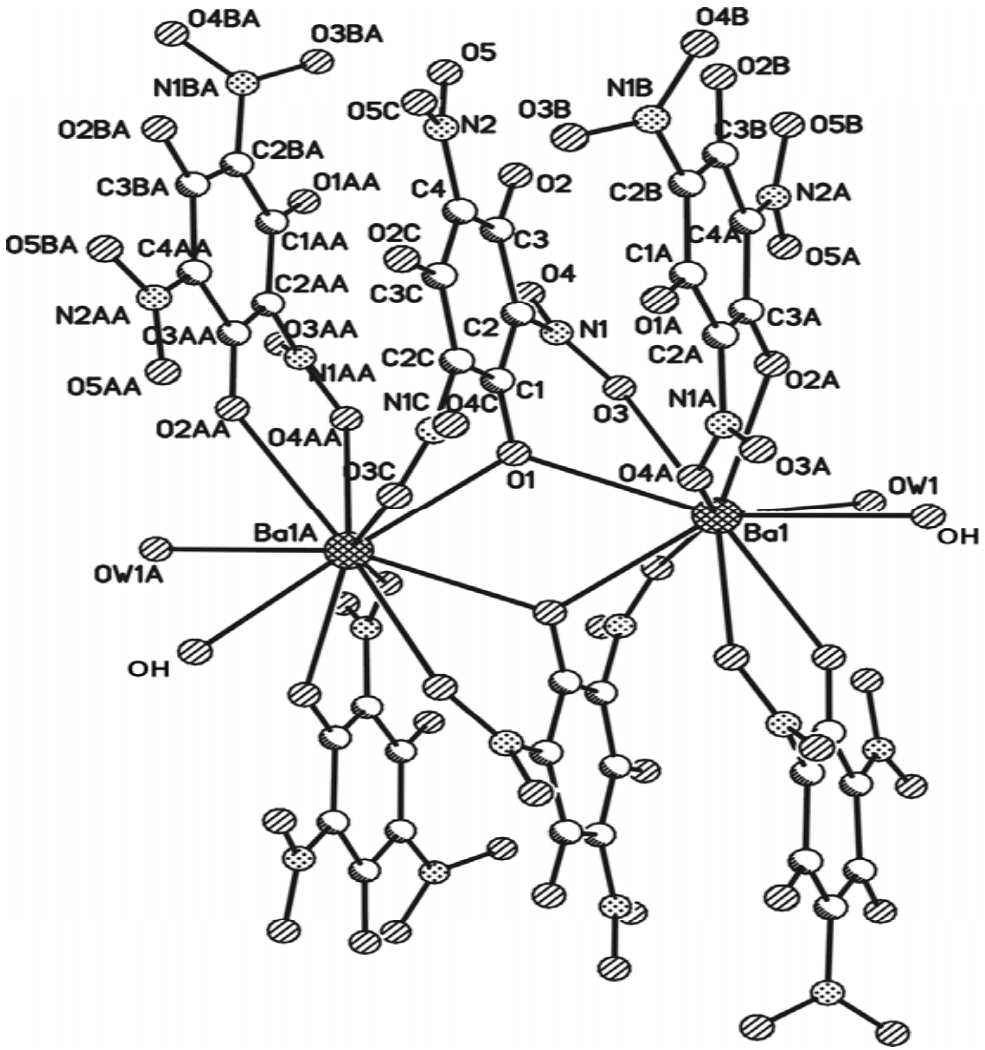
$[Rb(H_2TNPG)]_n$


O8
O9
N3
C7
C6
O7
O10
C8
O6
O7F
O7D
N4
C5
O7H
O5C
Rb
O8D
O3B
O2A
O2B
C4
C1
O10E
N2
O1
C3
C2
O5
O2
O4
N1
O3

$[Cs(H_2TNPG)]_n$



$[Ba_2(H_2TNPG)_2(H_2O)_2(OH)_2]$



Findings for polynitrophenols

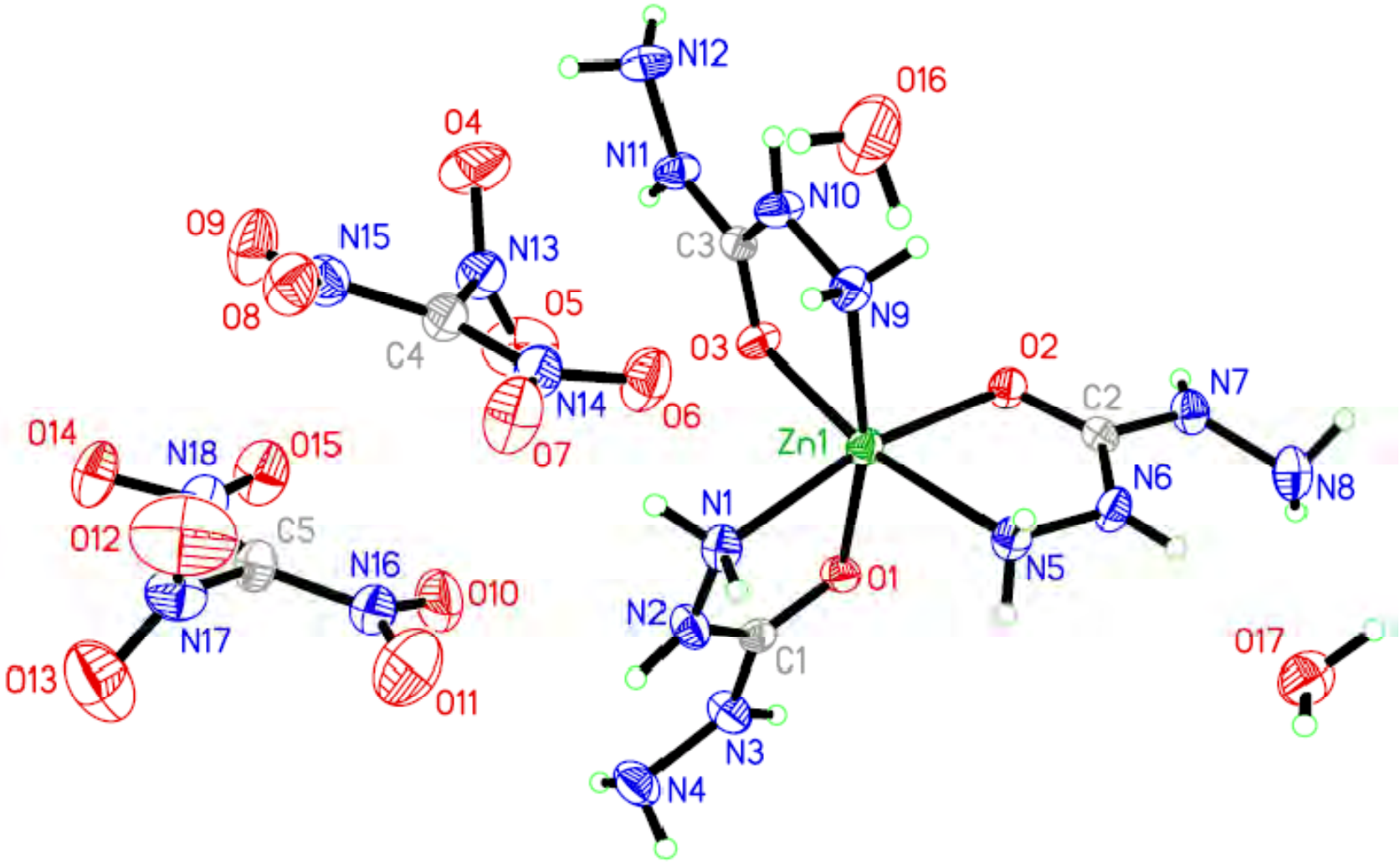
- **Experimental results verified TNPG showing trivalent state**
- **PA、TNR、TNPG served as anion and ligand in these compounds**
- **Coordination water and lattice water exist in the compounds and crystals**
- **PA 、 TNR 、 TNPG compounds exhibit powerful combustion and deflagration abilities**
- **Some of these compounds used as primary explosives and ignition compositions**

TNM

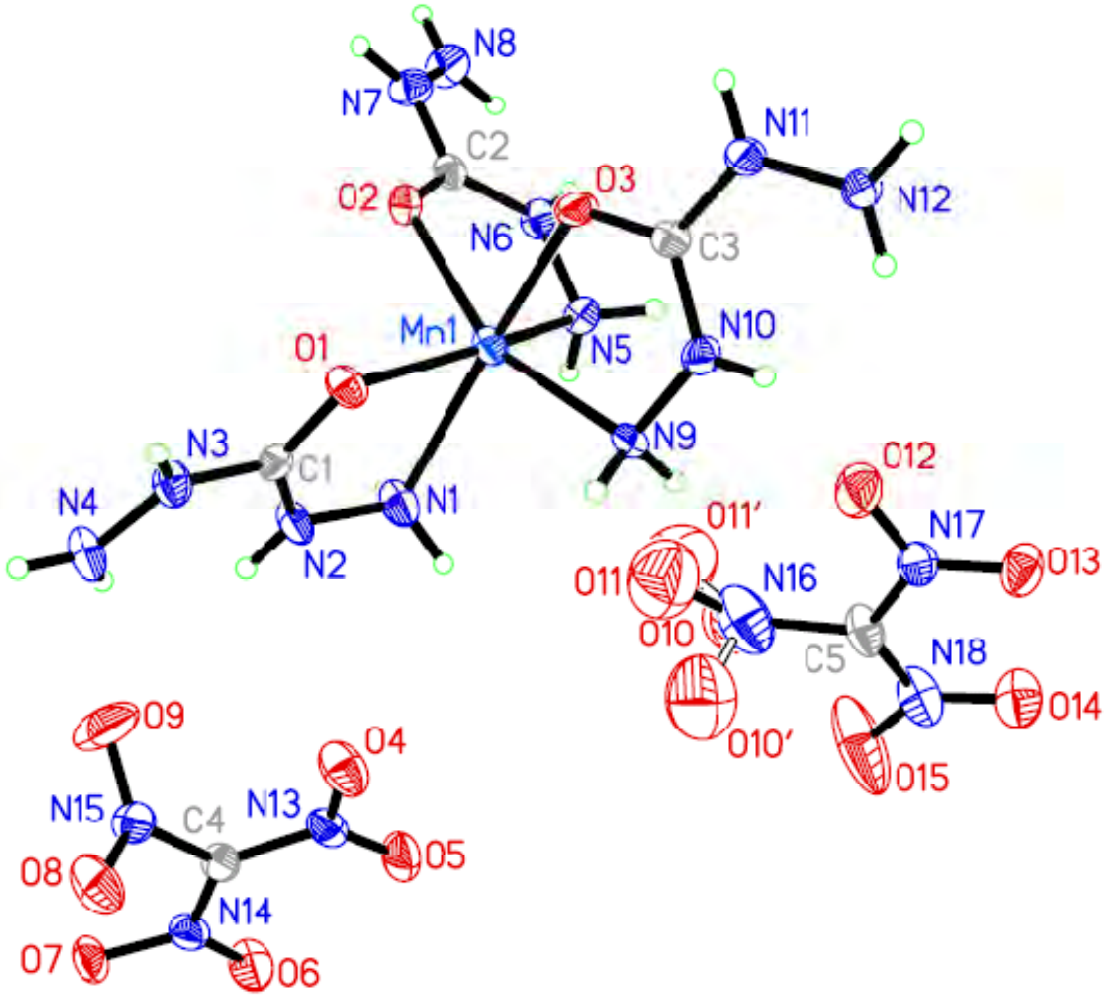
Trinitromethanate

Compounds

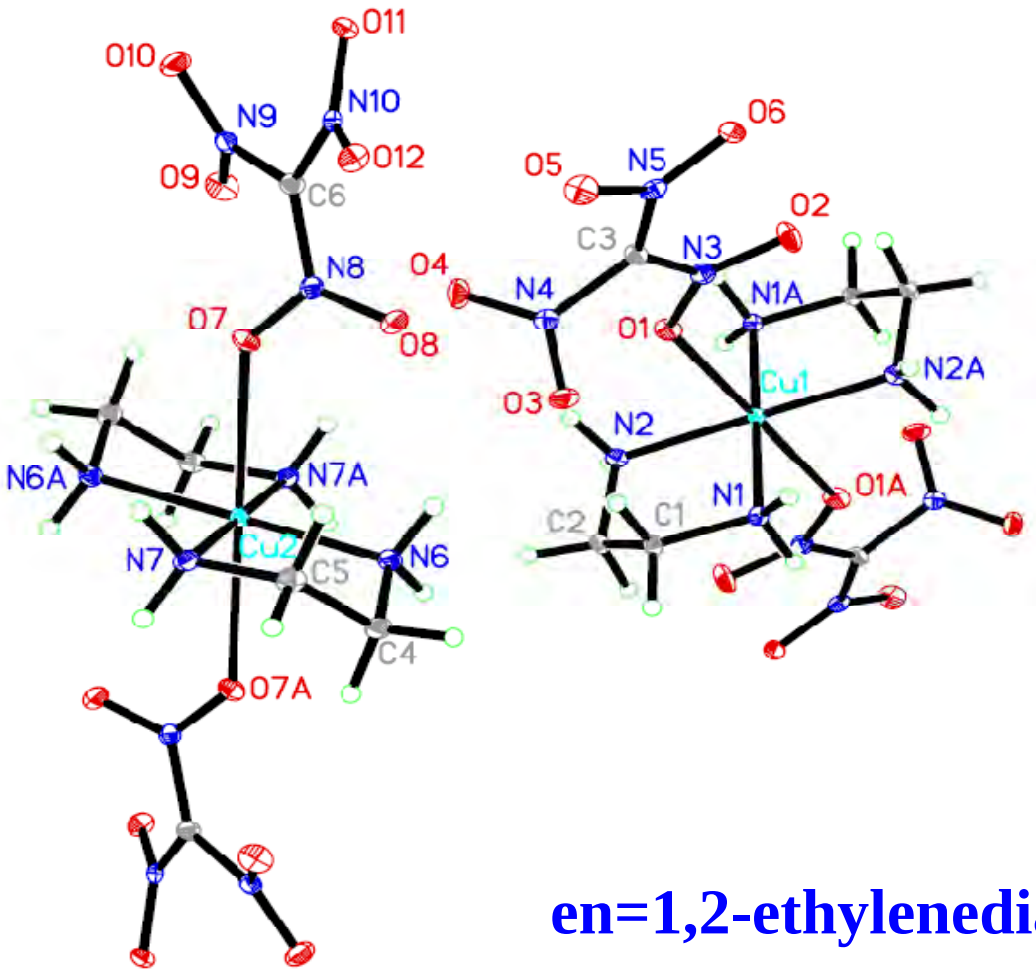
$[Zn(CHZ)_3](TNM)_2 \cdot 2H_2O$



$[Mn(CHZ)_3](TNM)_2$

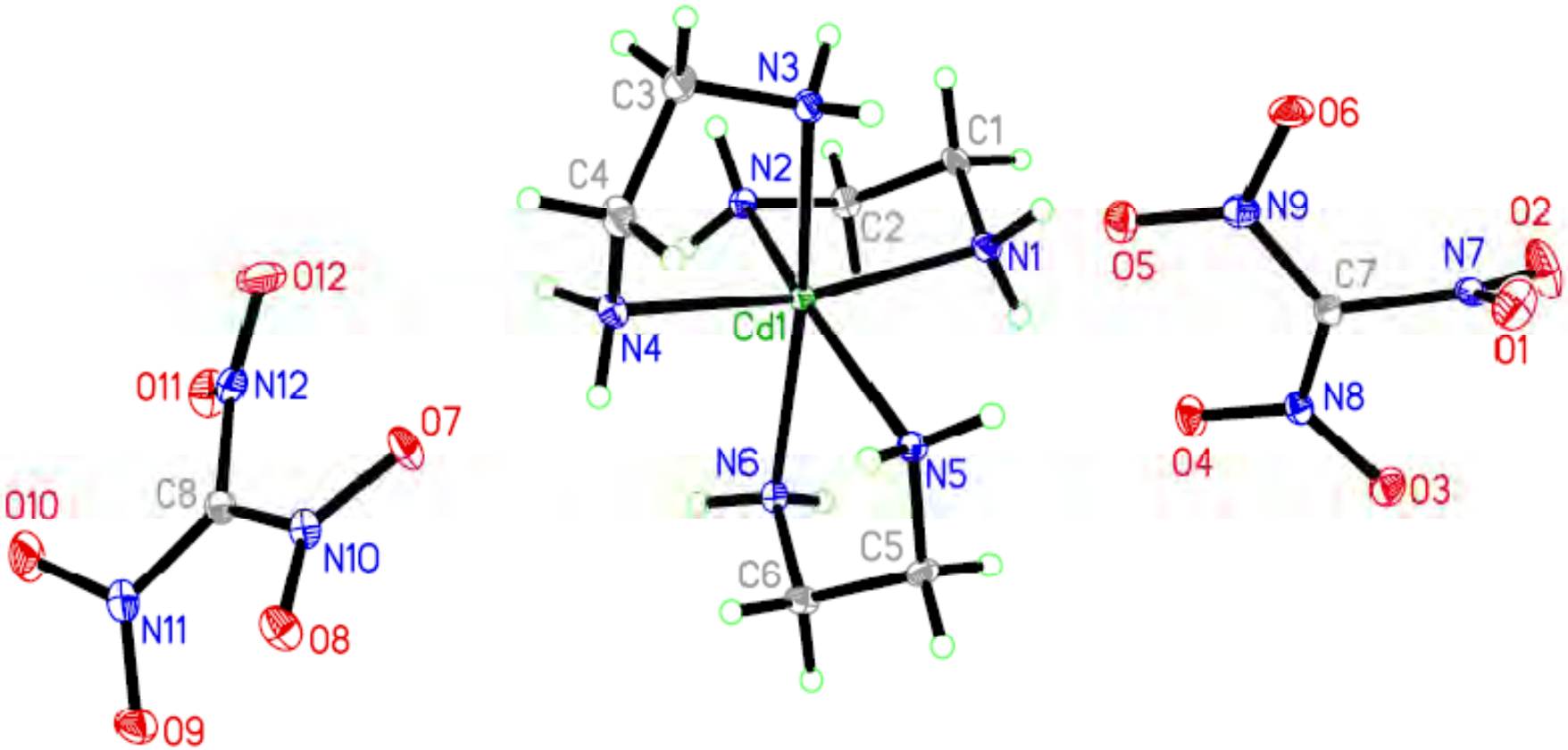

N8
N7
C2
O2
O3
N11
N12
N6
C3
Mn1
N5
N10
O1
N9
N3
C1
N4
N1
N2
O12
O11′
N17
O13
O11
N16
O10
C5
N18
O14
O10′
O15
O9
O4
N15
C4
N13
O5
O8
N14
O7
O6

$[Cu(en)_2(TNM)_2]$



en=1,2-ethylenediamine

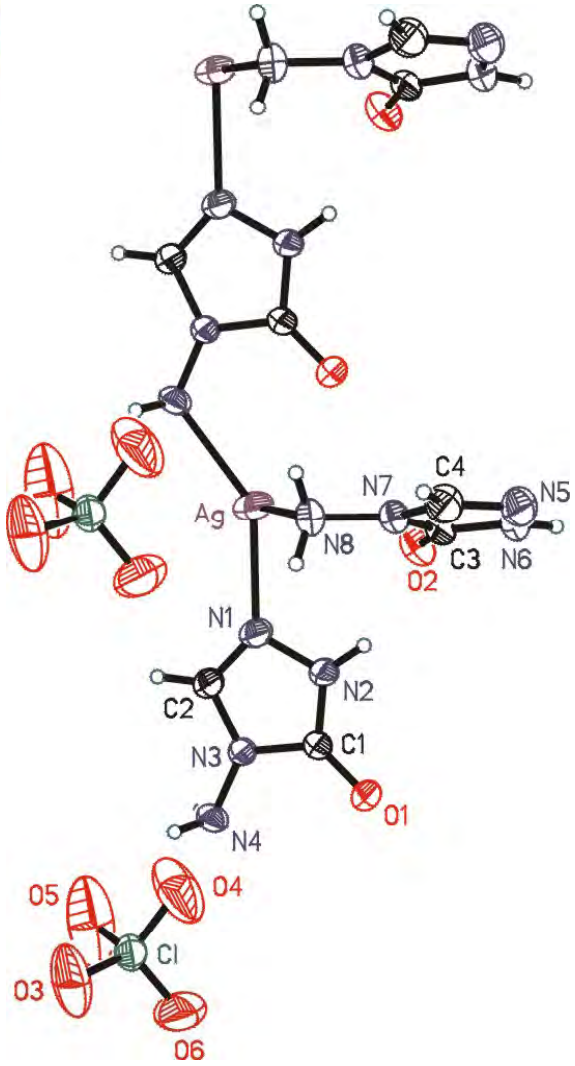
$[Cd(en)_3](TNM)_2$


O12
O11
N12
O7
O10
C8
N10
N11
O8
O9
C3
N3
C1
C4
N2
C2
N1
N4
Cd1
N6
N5
C6
C5
O6
N9
O2
O5
C7
N7
O1
N8
O4
O3

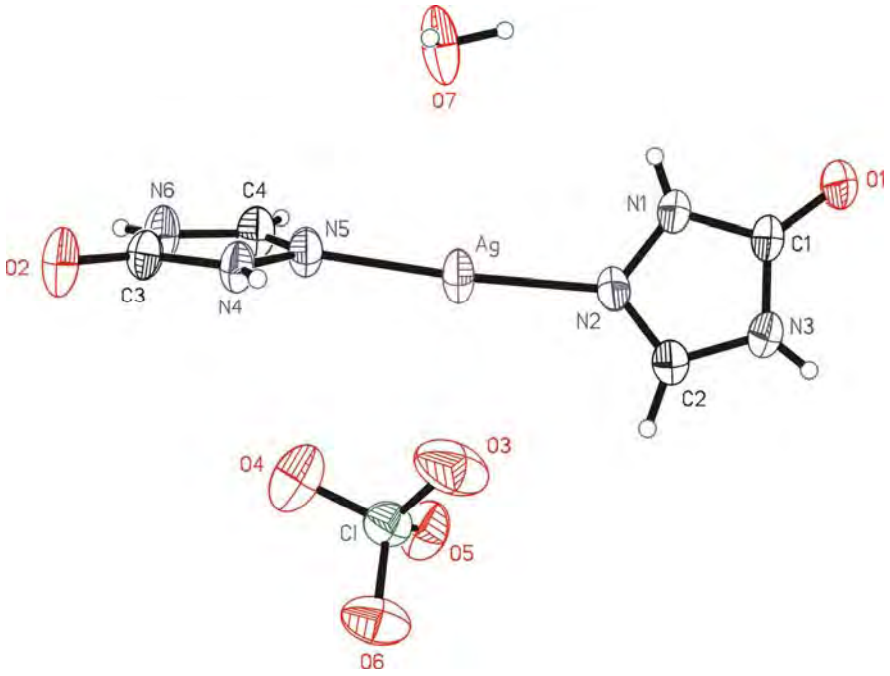
Results of Trinitromethanate

- Trinitromethane served mainly as anion not ligand in coordination compounds
- But Trinitromethane show as ligand only in copper compound
- There is no coordinate water and lattice water in this kind of compound
- Many of these compound possess high explosion ability and the decomposition temperature is lower than 150C
- Some of them might be used as primary explosive, ignition composition , oxidizer and oxidization additives.

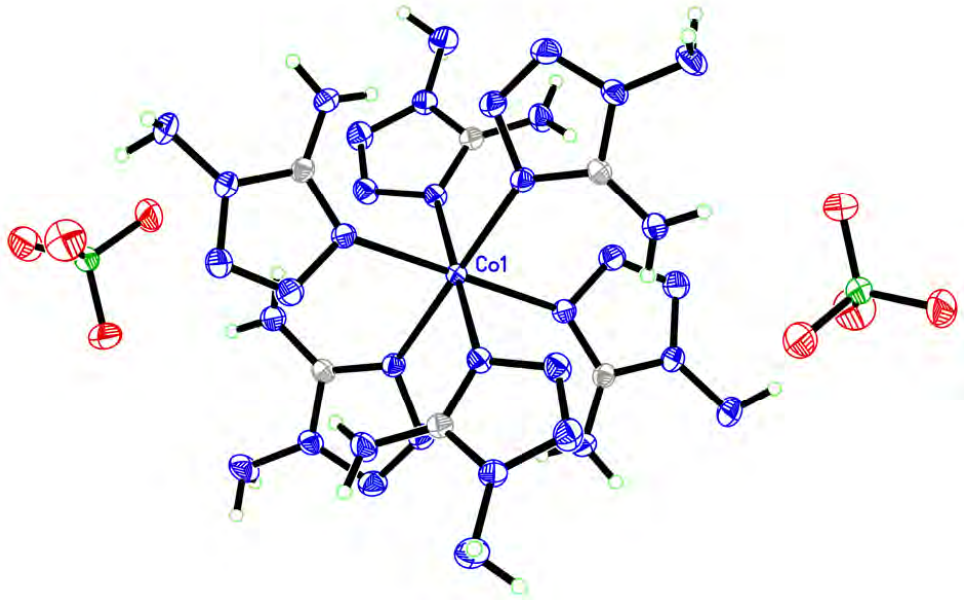
Perchlorate Compounds



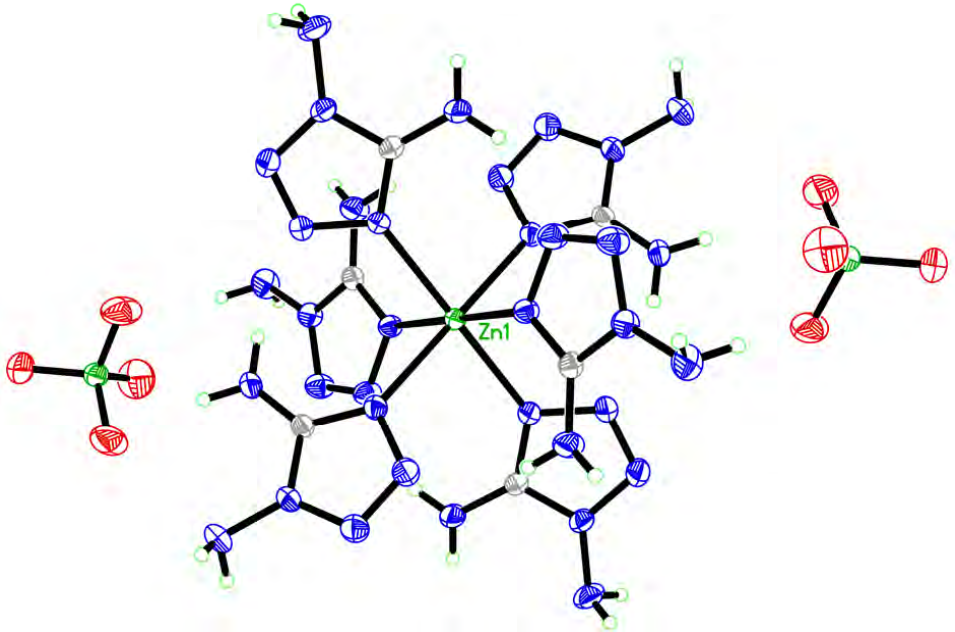
$\{[Ag(ATO)_2](ClO_4)\}_n$

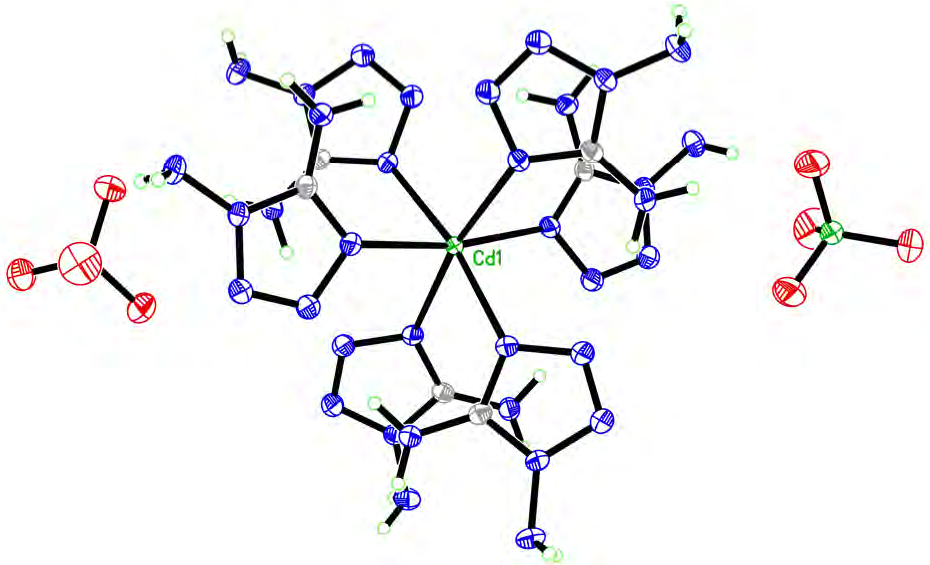


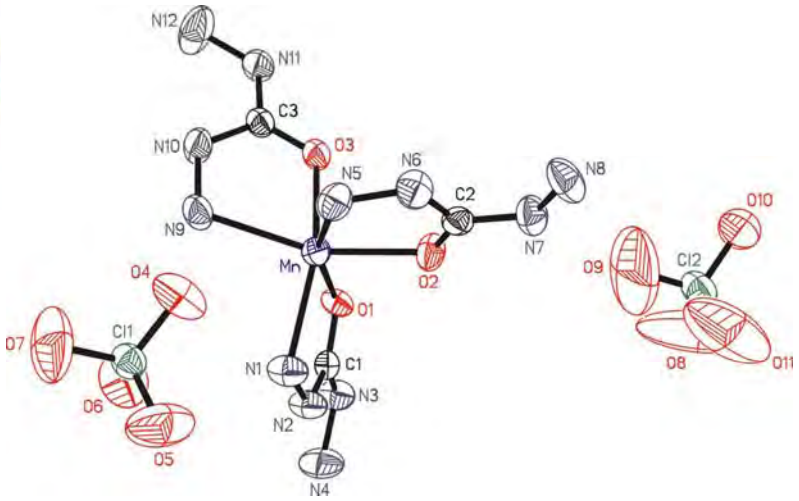
$[Ag(TO)_2](ClO_4)\cdot H_2O$



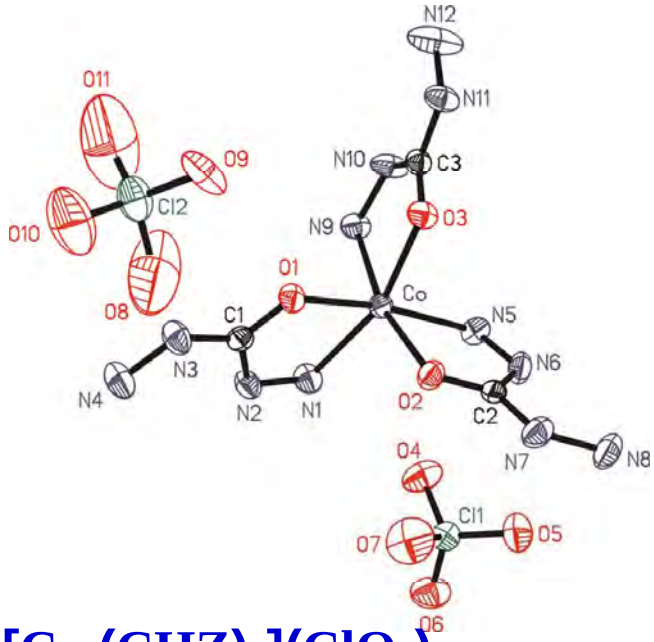
$[M(DAT)_6](ClO_4)_2$



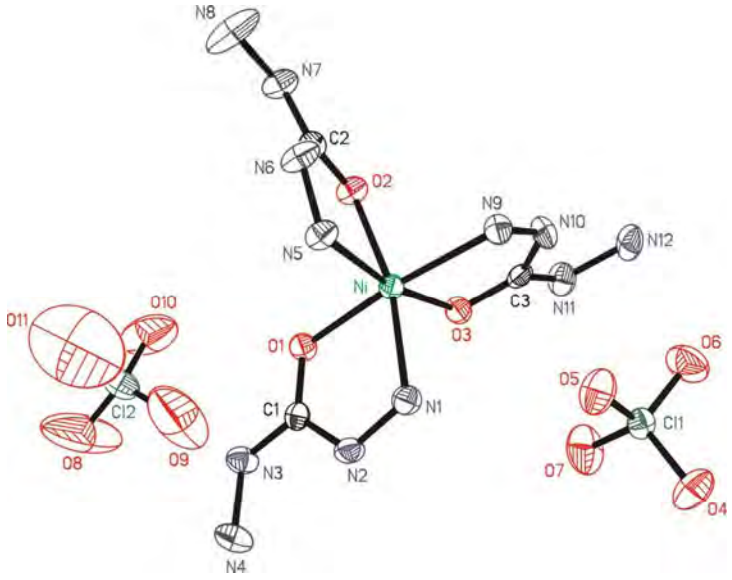




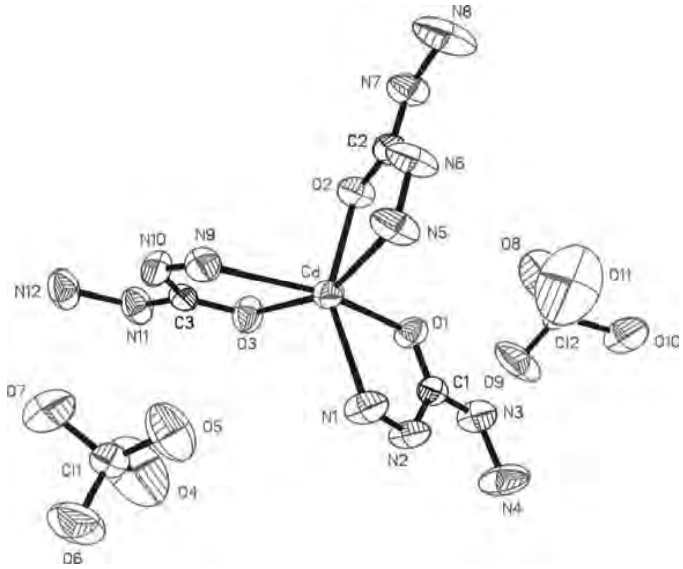
$[Mn\ (CHZ)_3](ClO_4)_2$



$[Co\ (CHZ)_3](ClO_4)_2$



$[Ni\ (CHZ)_3](ClO_4)_2$



$[Cd\ (CHZ)_3](ClO_4)_2$

Conclusions for Perchlorates

- **Perchlorate has the highest oxidization ability so that the compound show best explosive ability, many of them can be used as primary explosives**
- **For the carbohydrazide perchlorate, at least three five-member chelating ring formed in the coordination compounds. Therefore, this structure make the molecule more stable and exhibit low mechanic sensitivities**
- **Metal carbohydrazide perchlorates are perspective coordination compounds for exploring primary explosives.**

Achievements

- **Explored new molecules as many as 220**
- **Published 300 articles**
- **5 kinds of new compounds have been found the application industrially**
- **Many awards from the government**

Thanks From our Group

Prof. Qiao Ph.D

Prof. Yang Ph.D.

Ass. Prof. Zhang Ph.D.

Researcher Zhou Ph.D.

Thanks all of you very much

Welcome to visit us

Beijing Institute of Technology