BUILDING UP OF OPEN – FRAMEWORK MATERIALS

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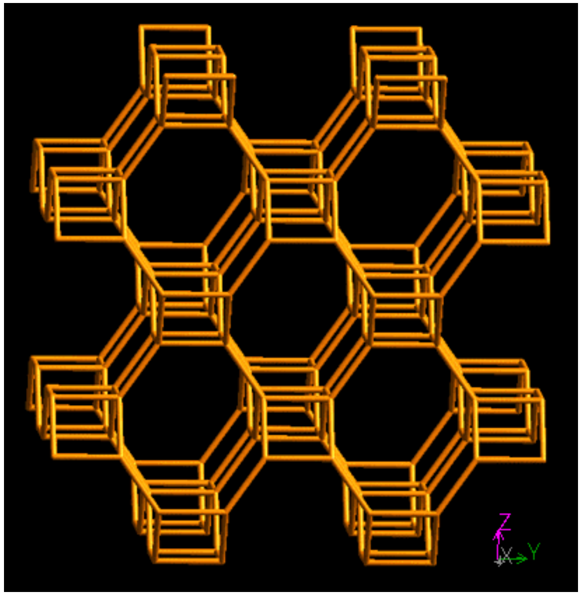
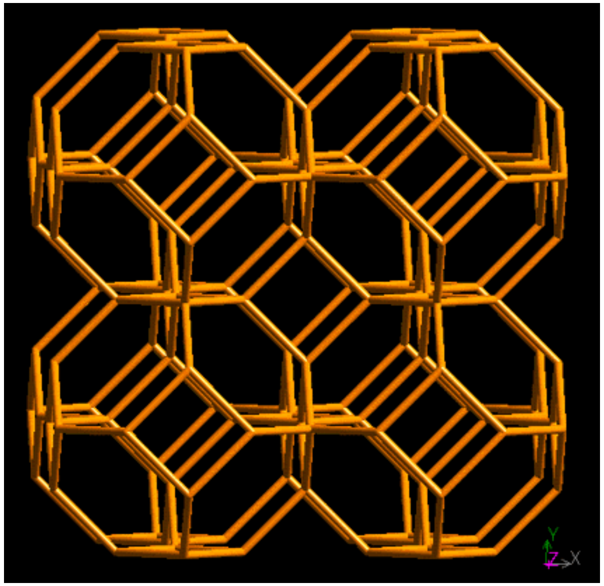
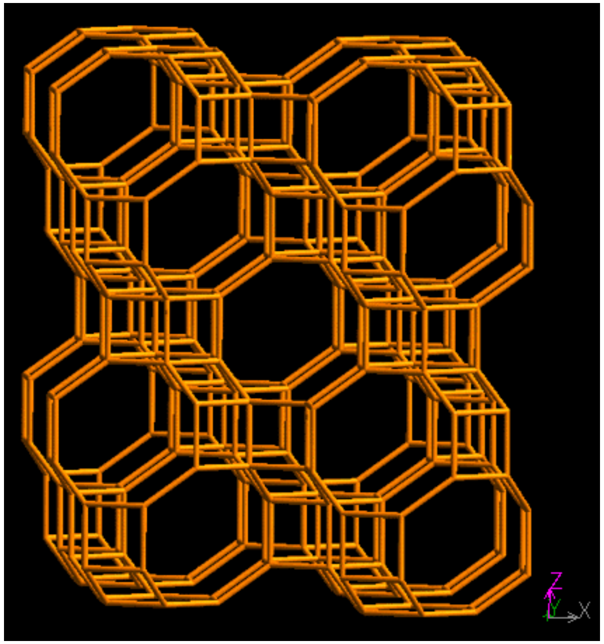
Zeolites



Gismondine



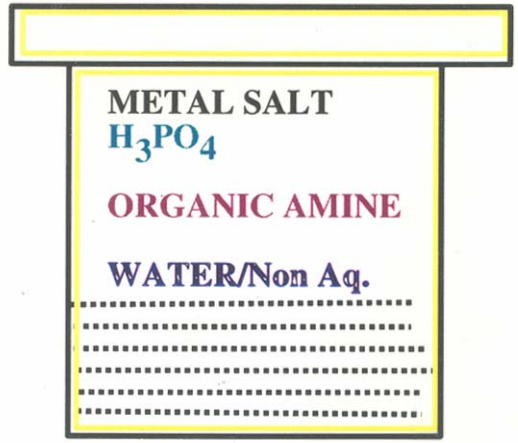
Sodalite



Chabazite

OPEN – FRAMEWORK PHOSPHATES

HYDROTHERMAL SYNTHESIS



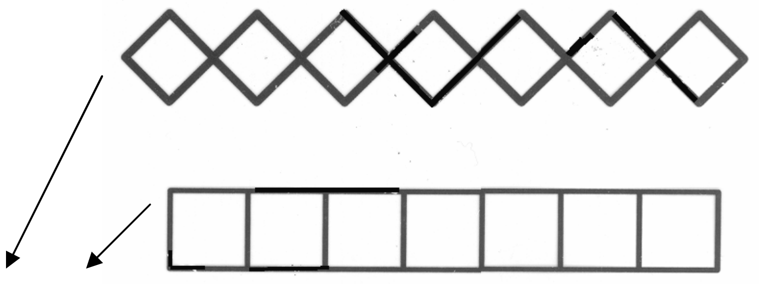
HIERARCHY OF STRUCTURES

Zero – Dimensional (Monomer)

One – Dimensional (Chain / Ladder)

Two – Dimensional (Layer)

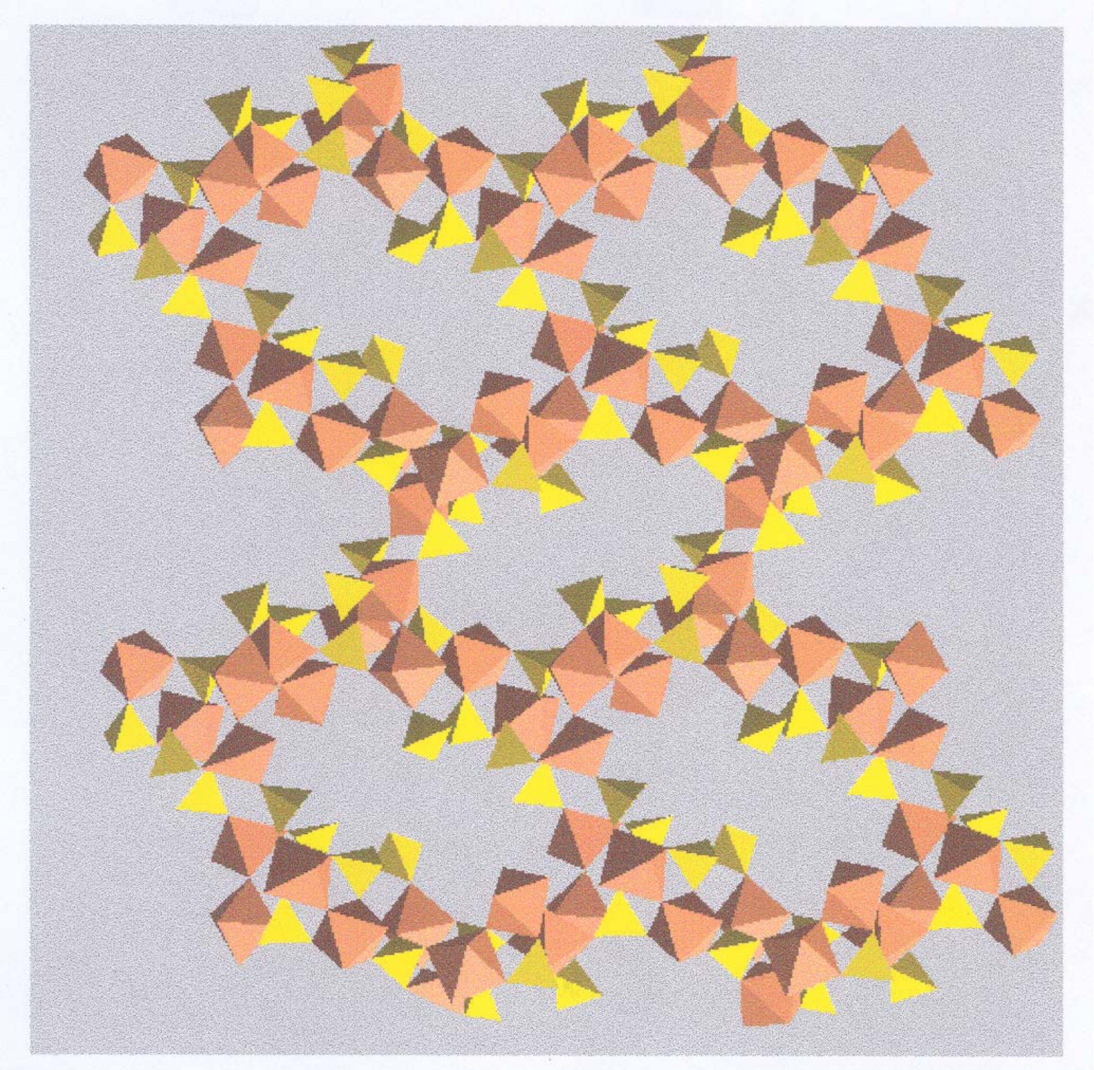
Three – Dimensional



Linear Chain (CS 4-membered rings)

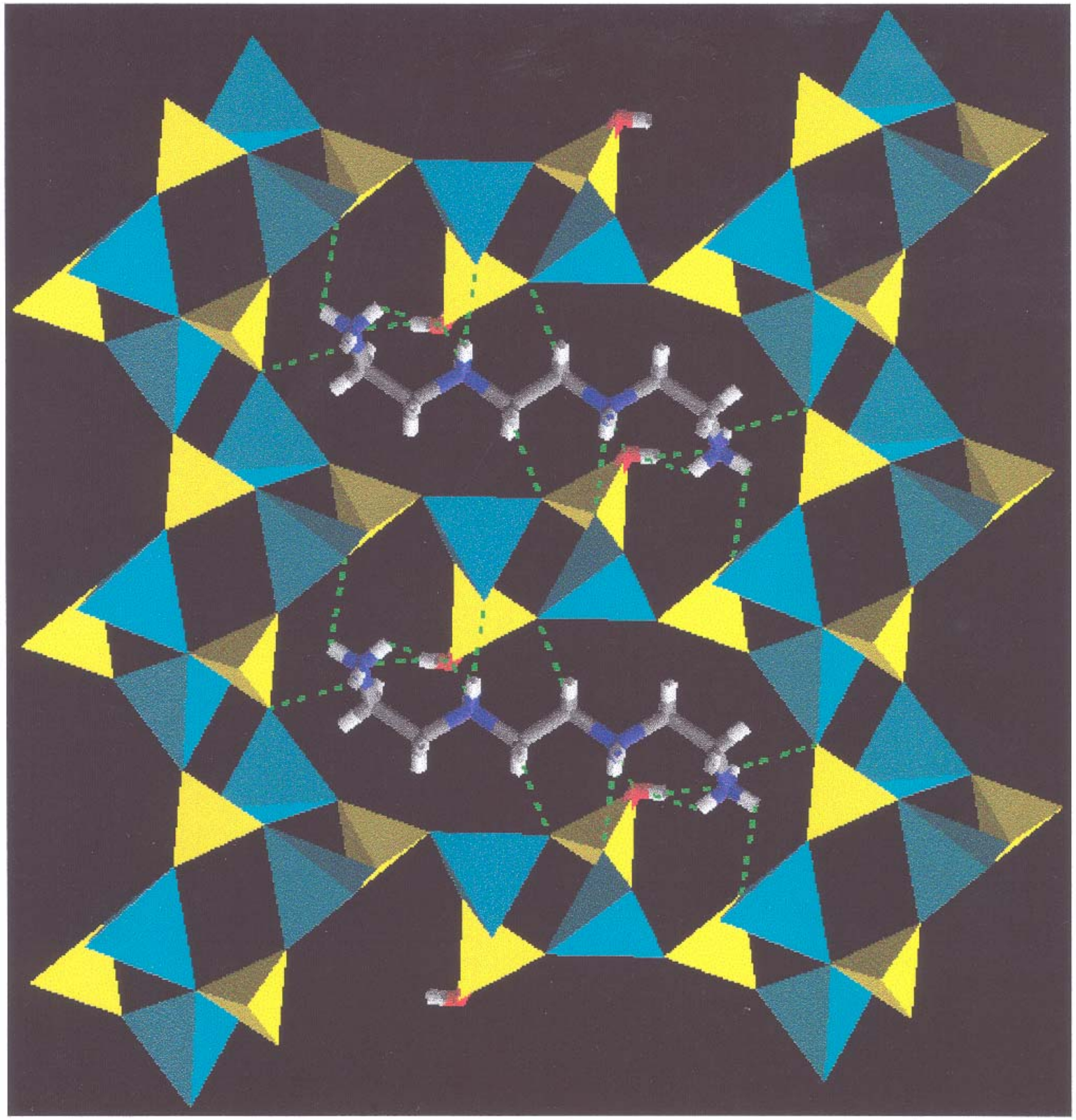
Ladder (ES 4-membered rings)

NOTE THE 4-MEMBERED RING



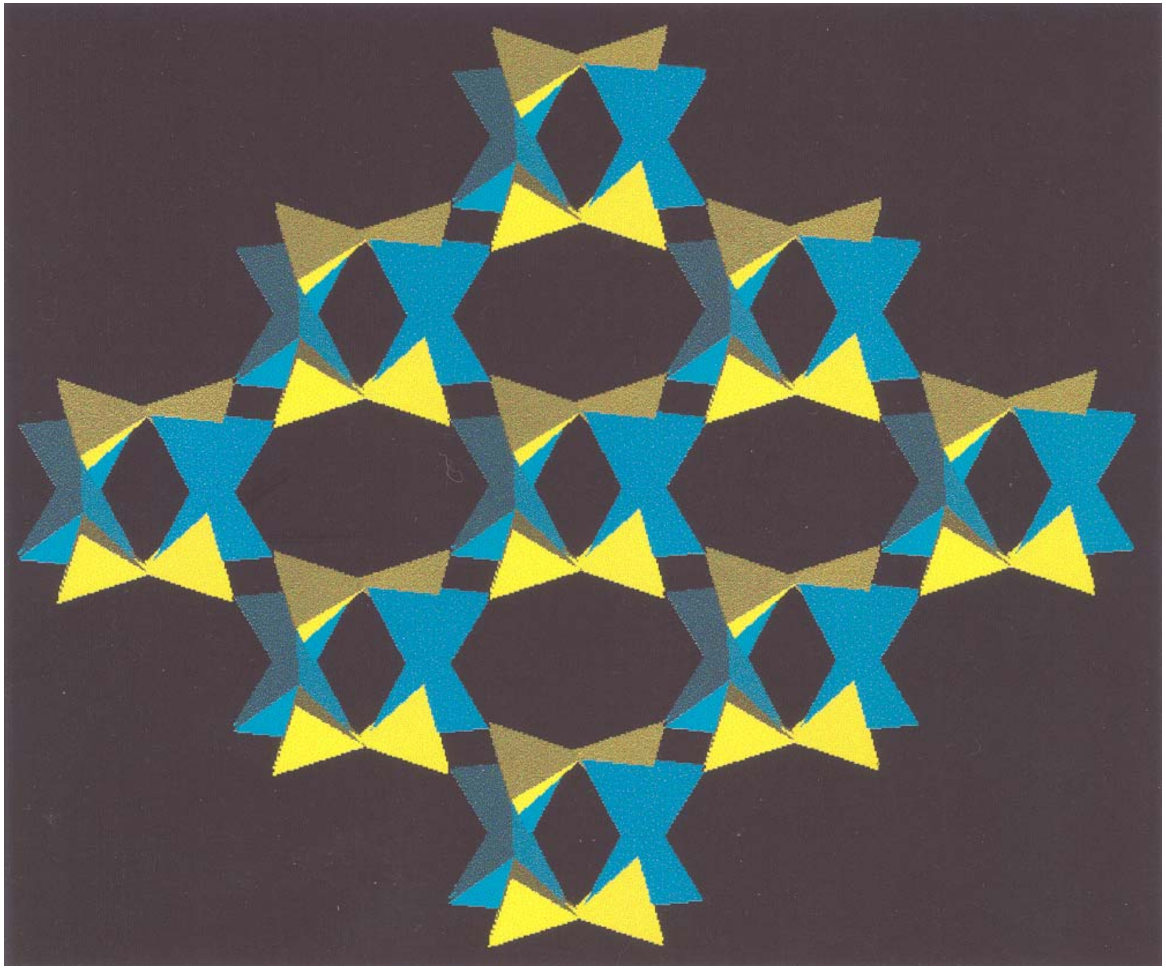
A 3D iron phosphate, $[C_4N_3H_{16}]_2$ $[Fe_5F_4(H_2PO_4)(HPO_4)_2(PO_4)_4]\cdot 0.5H_2O$, with 18-membered channel. (Brick red-FeF_xO_{6-x} octahedra, yellow-PO_4 tetrahedra)

A. Choudhury, S. Natarajan, C. N. R. Rao, *Chem. Commun.*, 1999, 1305.



A three-dimensional (3D) zinc phosphate, [$C_6N_4H_{22}]_{0.5}[Zn_3(PO_4)_2(HPO_4)]$, with 16-membered S-shaped channel. (Light blue-ZnO_4, yellow-PO_4 tetrahedra)

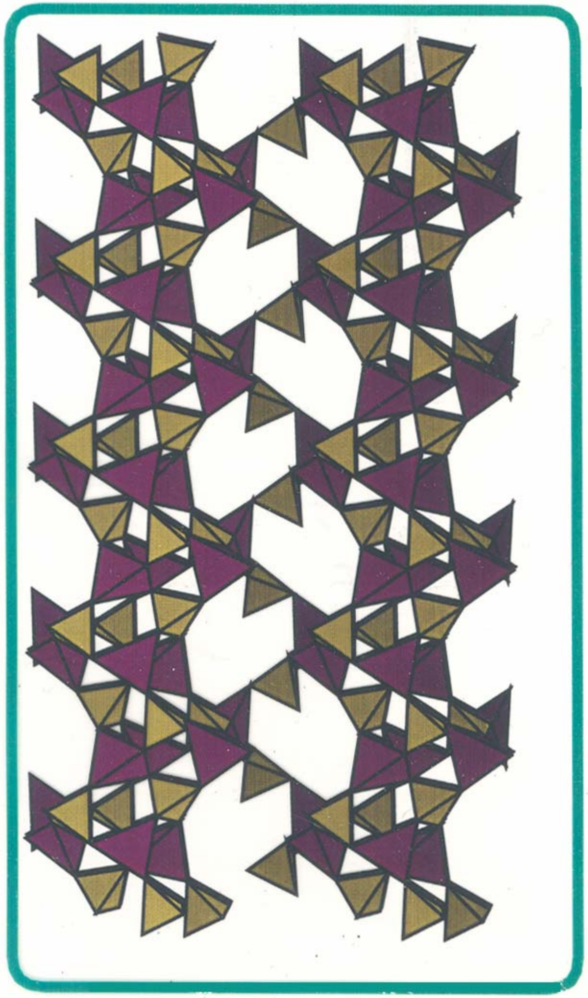
A. Choudhury, S. Natarajan, C.N.R. Rao, *Inorg. Chem*. 2000, *39*, 4295**.**



A 3D zinc phosphate, $[C_2N_2H_{10}]_{0.5}[Zn(PO_4)]$, analogous to the zeolite gismondine (GIS), possessing 8-membered channels in all the three crystallographic directions. (Light blue-ZnO_4, yellow-PO_4 tetrahedra)

A. Choudhury, S. Neeraj, S. Natarajan, C.N.R. Rao,
J. Mater. Chem. 2001, *11*, 1537.

Chiral Zinc Phosphate with Intersecting Helical Channels



Structure made from 4-, 6-, and 8-membered rings to form Helices

Hydrothermal Synthesis
150 C/5d
Large Needle-like Crystals

Composition and Time of the reaction is important for forming the phase and longer duration forms different phase

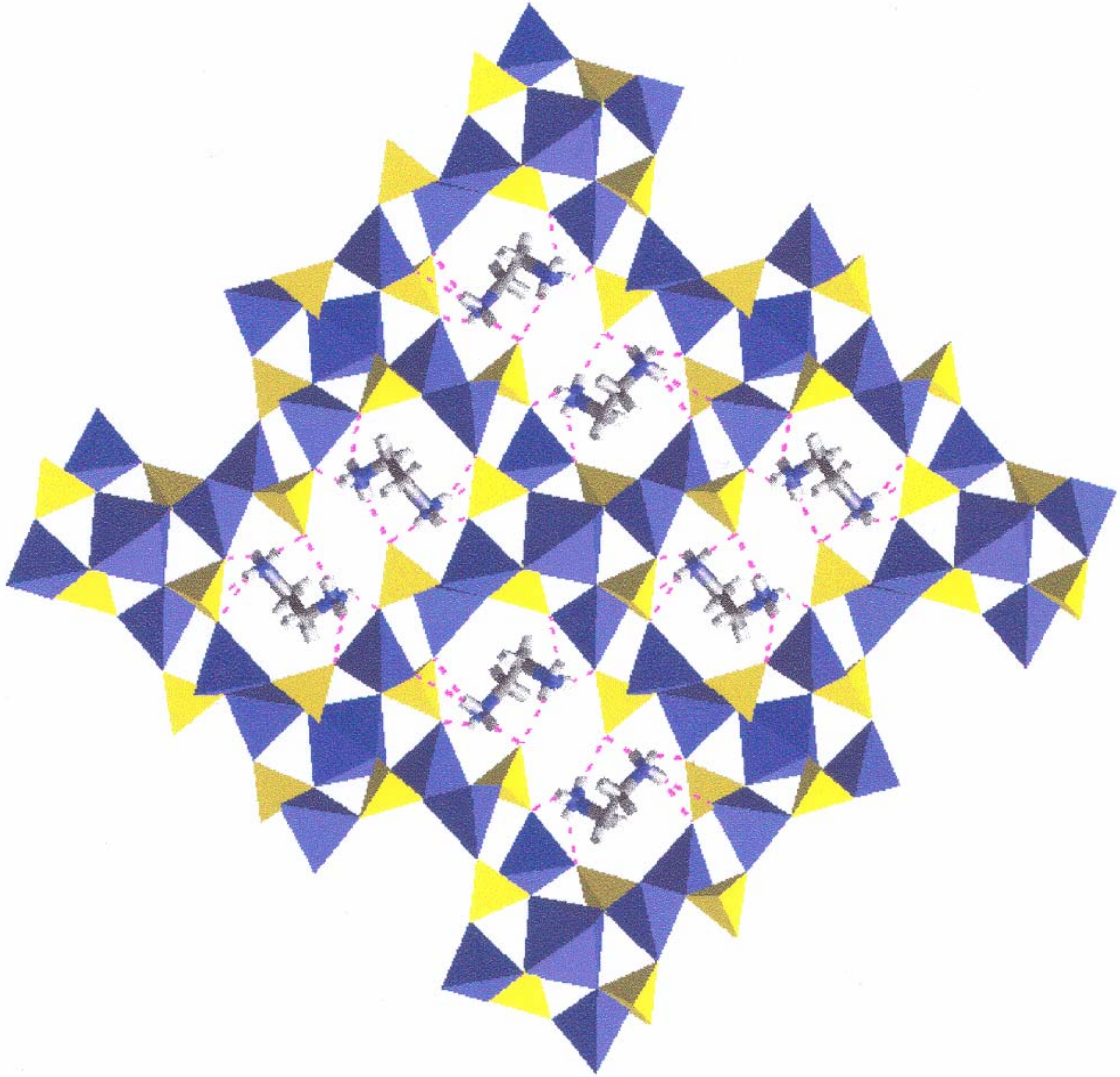
a = 10.021(1)
b = 9.286(1)
c = 11.856(1)
β = 103.1

V= 958.7

Z= 9

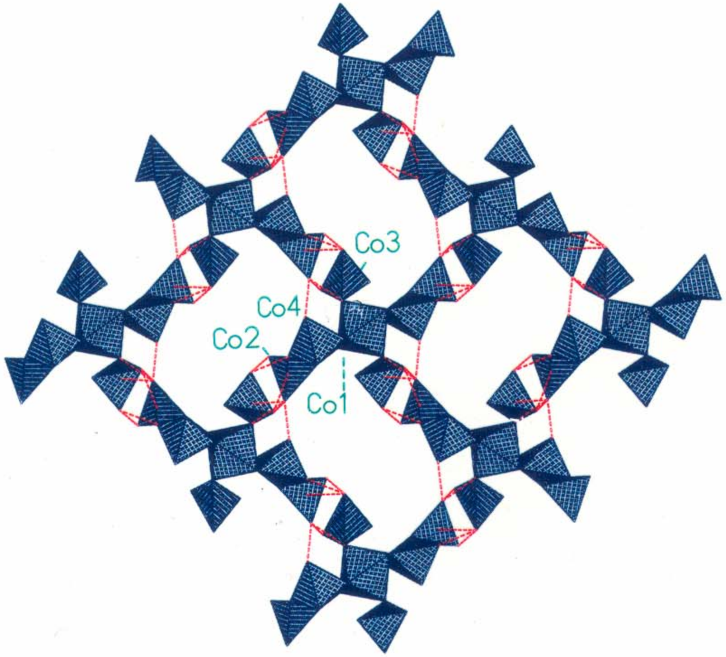
P21

S. Neeraj, S. Natarajan & C. N. R. Rao
Chem. Commun. 1999, 165

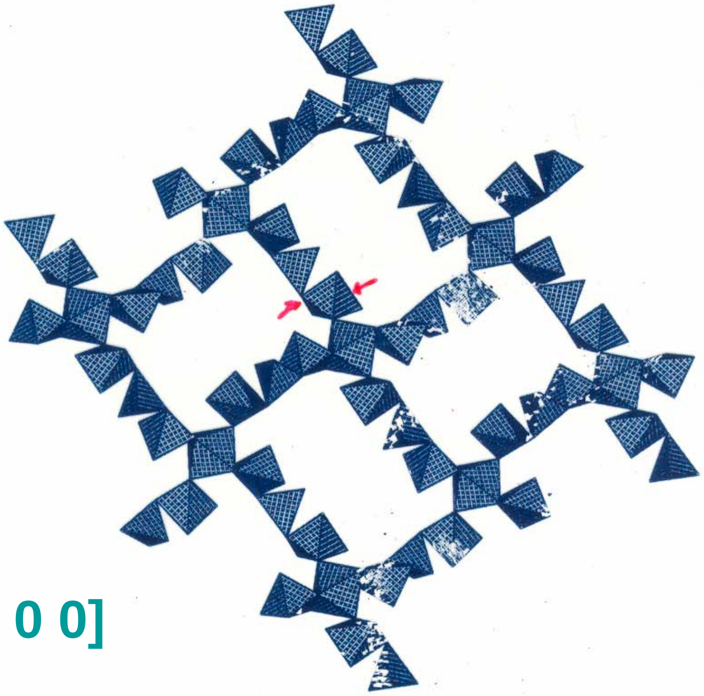


A 3D cobalt phosphate, $[C_2N_2H_{10}][Co_{3.5}(PO_4)_3]$, with 12-membered channel. (Blue-CoO_x polyhedra, yellow-PO_4 tetrahedra)

A. Choudhury, S. Neeraj, S. Natarajan, C. N. R. Rao, *Angew. Chem. Int. Ed*. 2000, *39*, 3091.

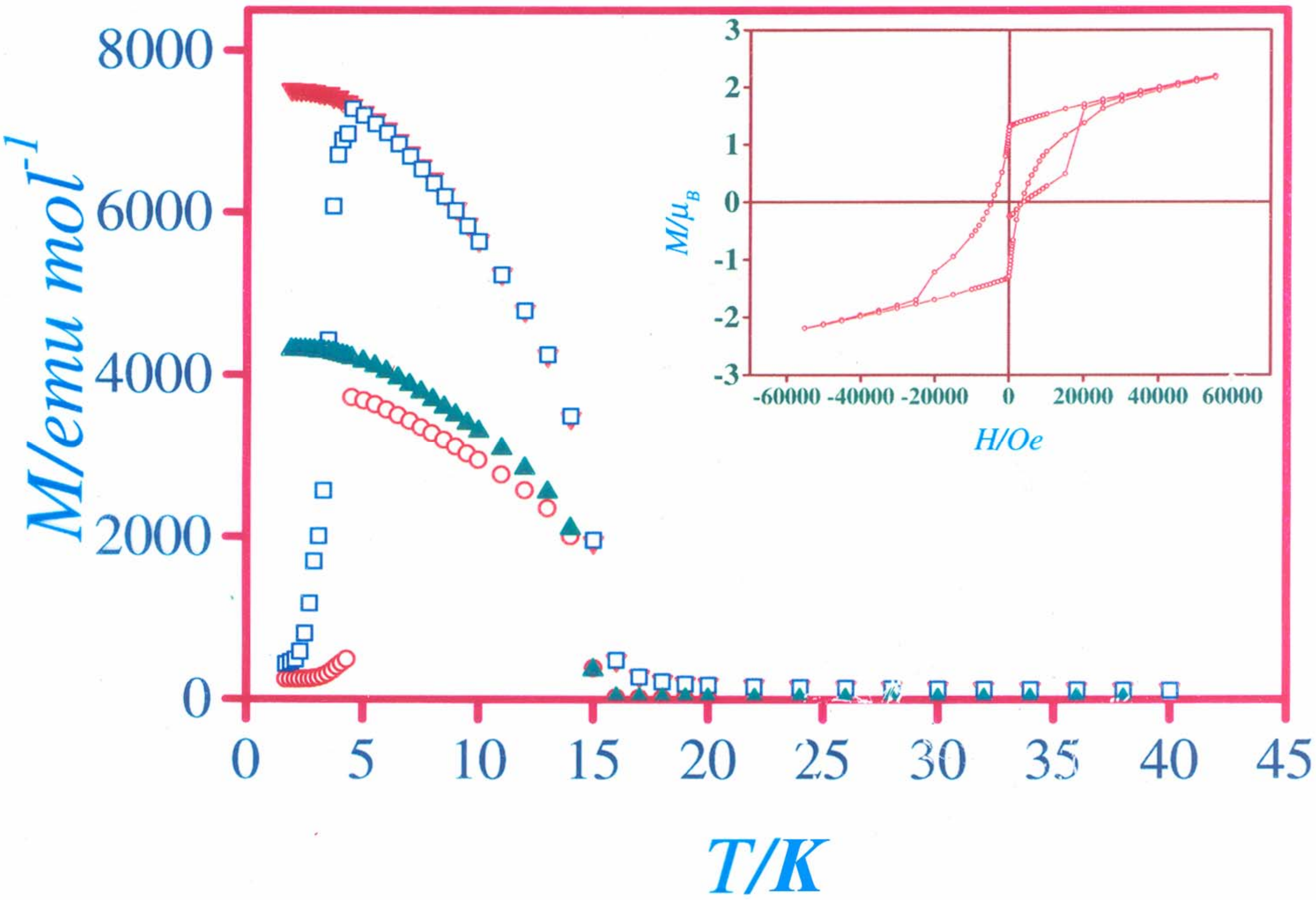


293K

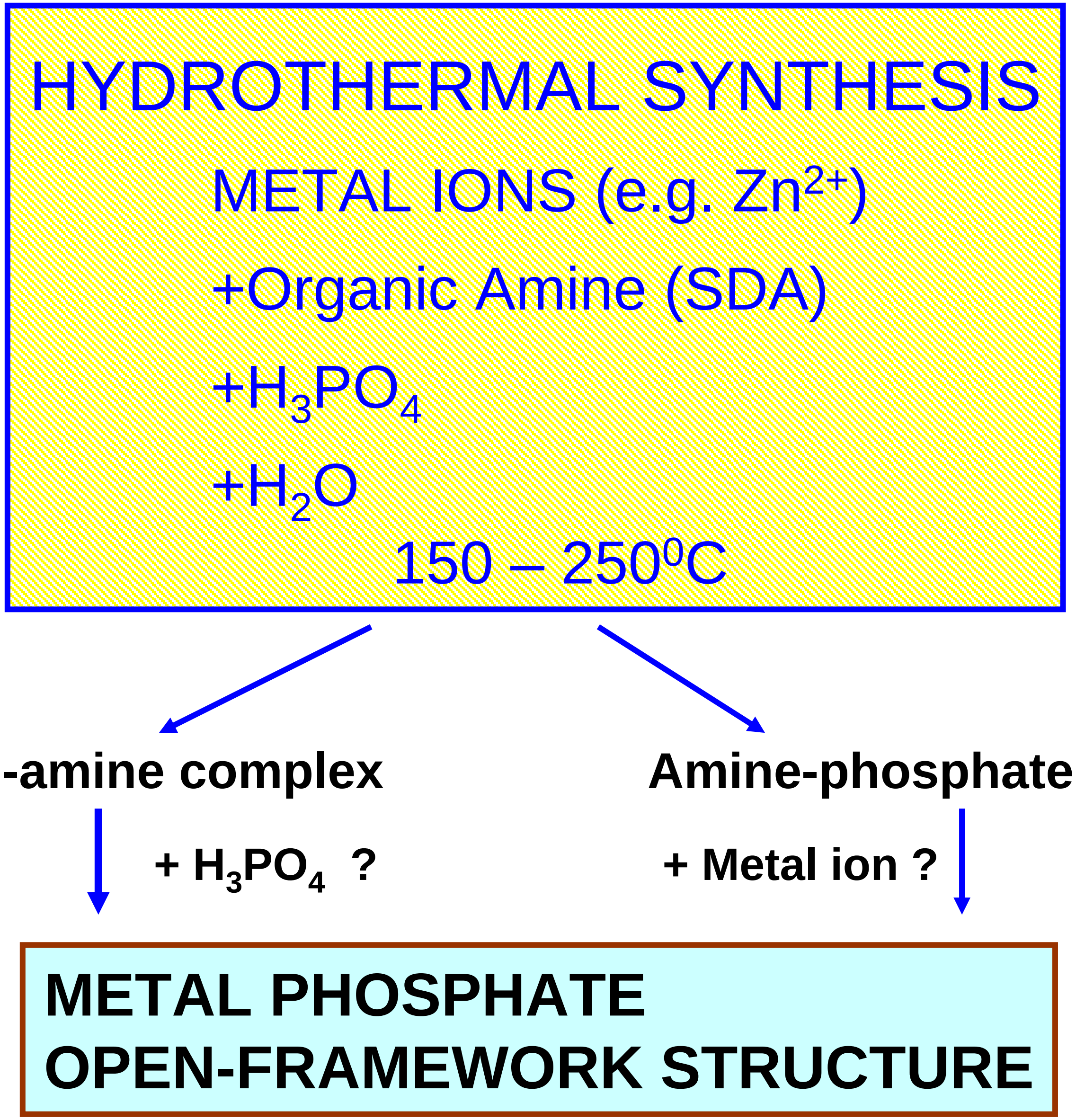


140K

along [1 0 0]


M/emu mol^{-1}
8000
6000
4000
2000
0
0
5
10
15
20
25
30
35
40
45
T/K
M/μ$_B$
3
2
1
0
-1
-2
-3
-60000
-40000
-20000
0
20000
40000
60000
H/Oe

WHAT IS THE SECRET OF THE MYRAID OF OPEN-FRAMEWORK PHOSPHATES!!



HYDROTHERMAL SYNTHESIS

METAL IONS (e.g. Zn^{2+})

+Organic Amine (SDA)

$+H_3PO_4$

$+H_2O$

$150 – 250^0C$

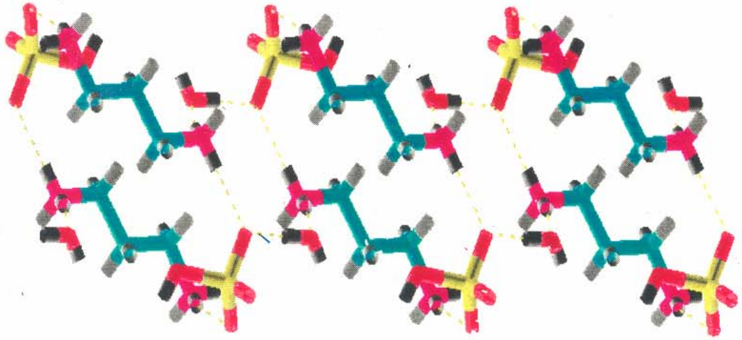
Metal-amine complex

+ H_3PO_4 ?

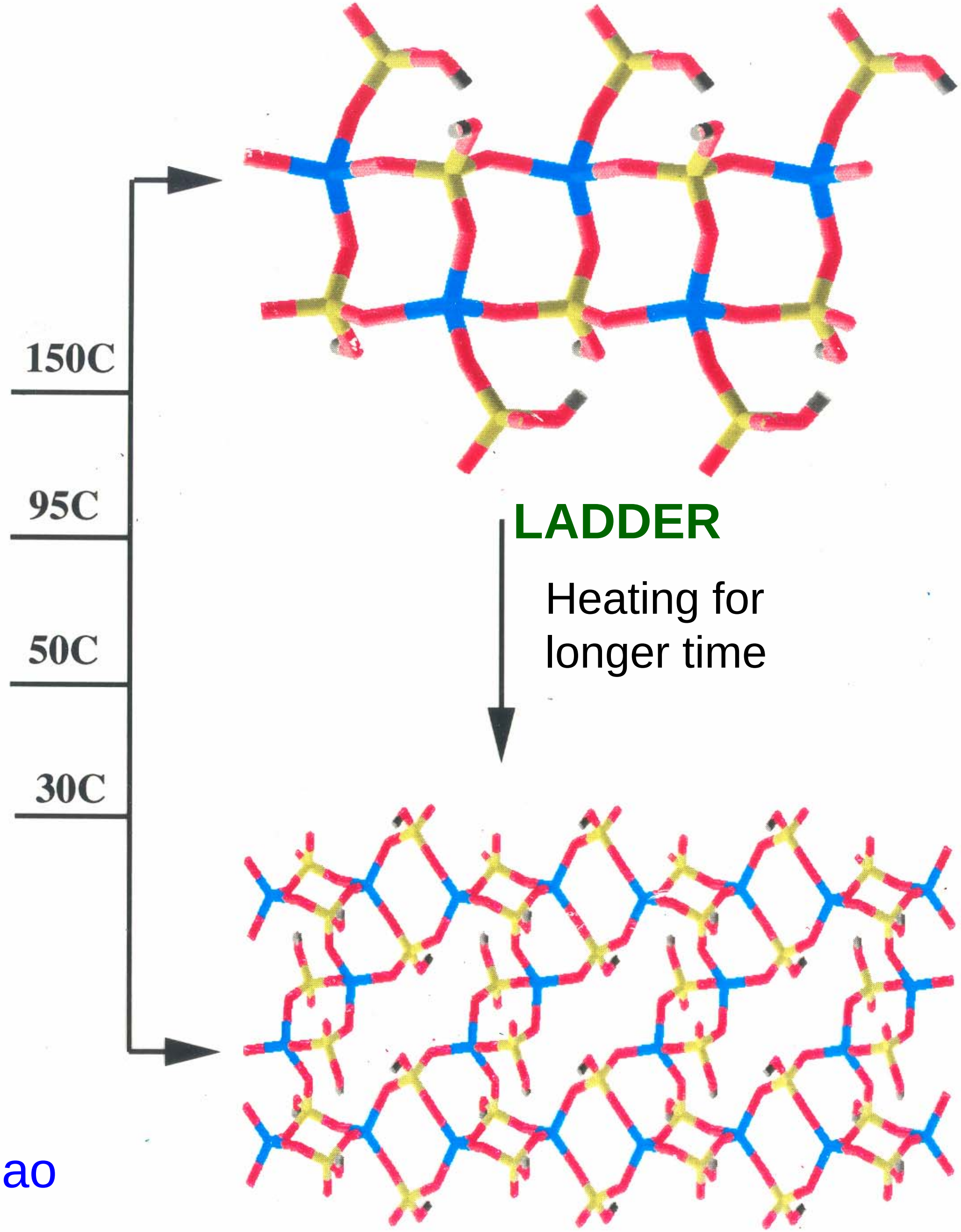
Amine-phosphate

+ Metal ion ?

METAL PHOSPHATE
OPEN-FRAMEWORK STRUCTURE



1,3- DIAMINOPROPANE HYDROGEN PHOSPHATE



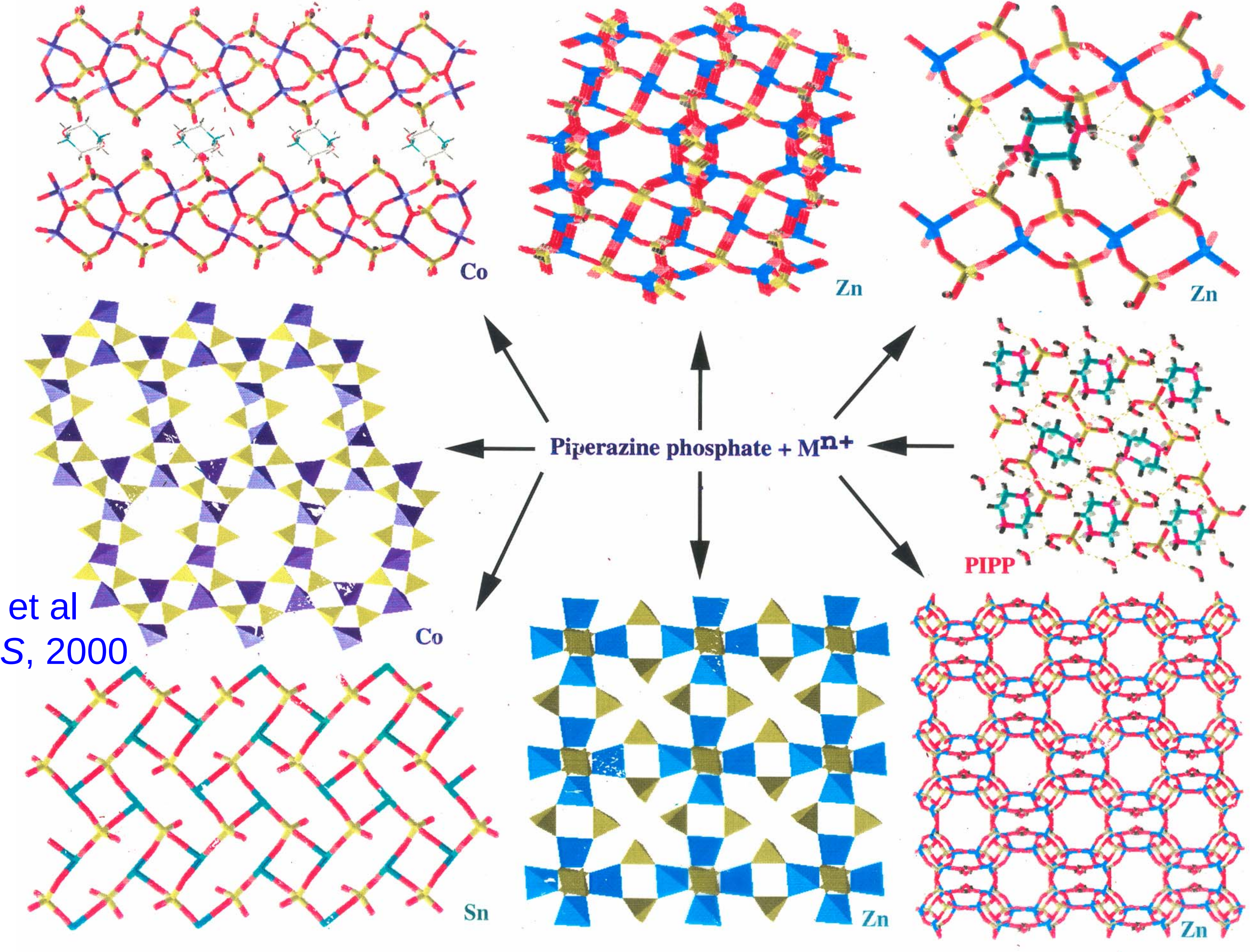
LADDER

Heating for longer time

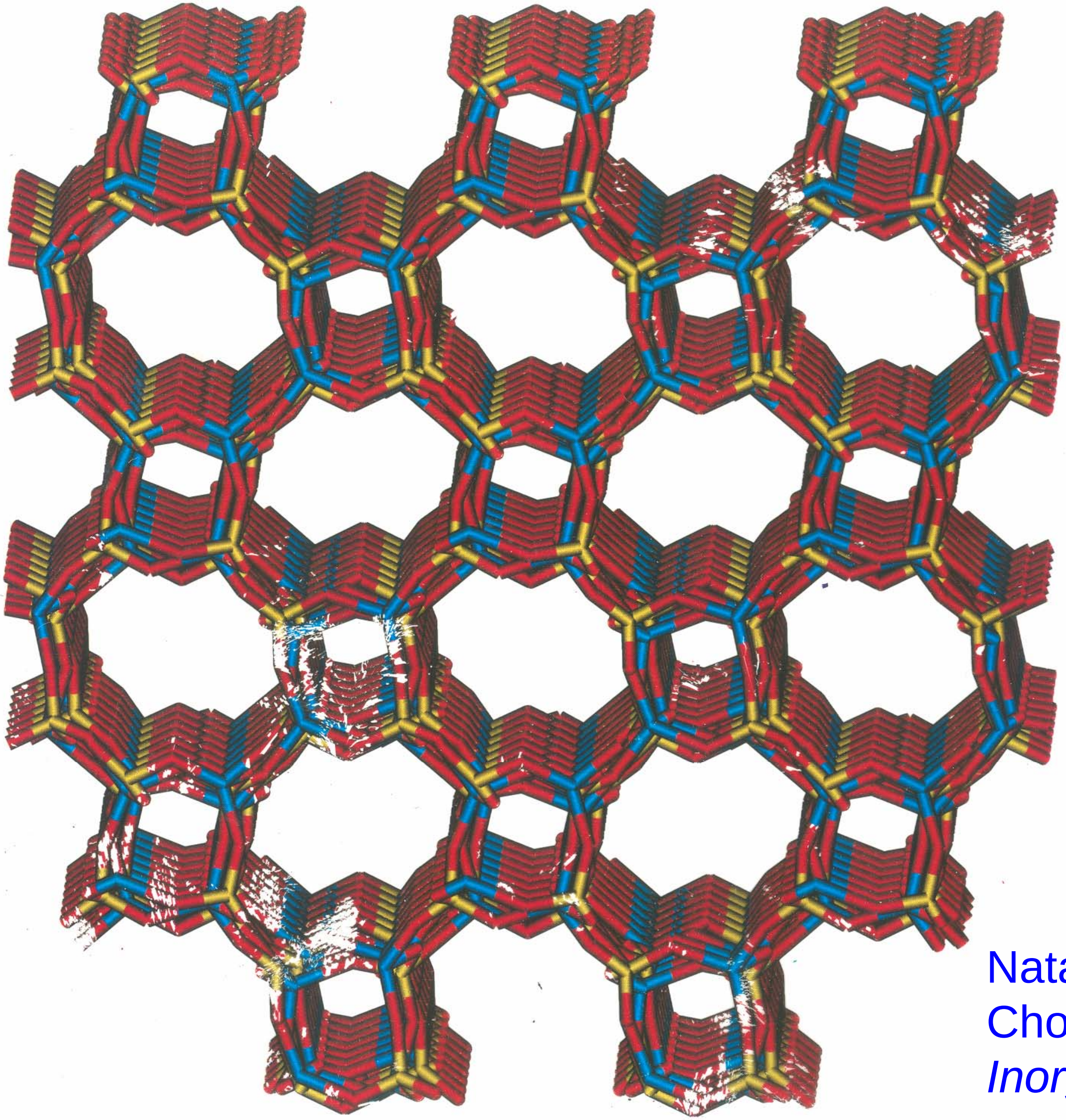
LAYER

S. Neeraj, S. Natarajan & C. N. R. Rao
Angew. Chem., 1999, 38, 3480

Amine Phosphate route to Open-framework metal phosphates



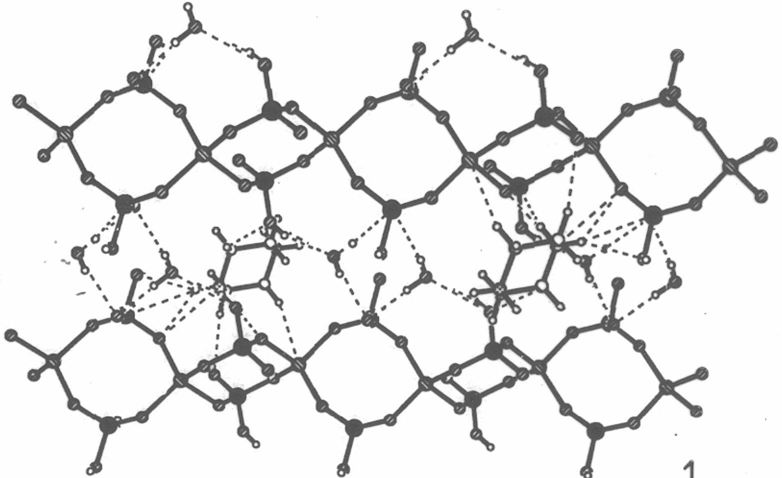
Rao et al
JACS, 2000



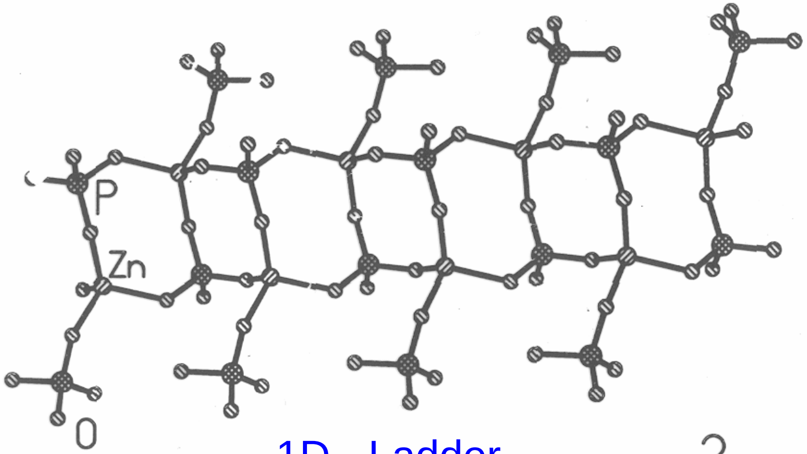
Natarajan, Neeraj,
Choudhury & Rao
Inorg. Chem., 2000

Zeolitic Co Phosphate (EDA)

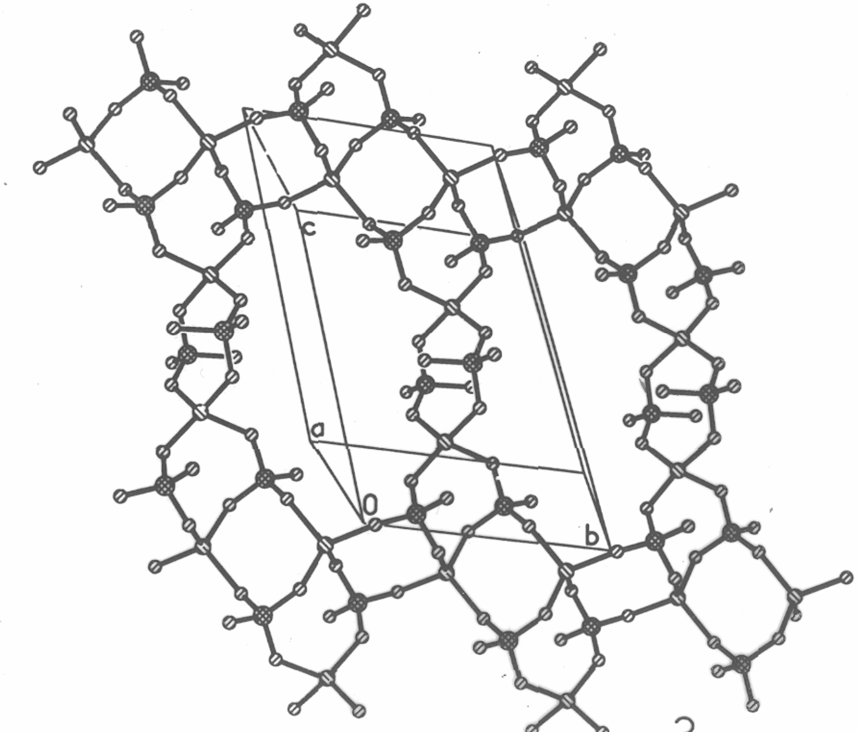
Zn Phosphates of Different Dimensionalities



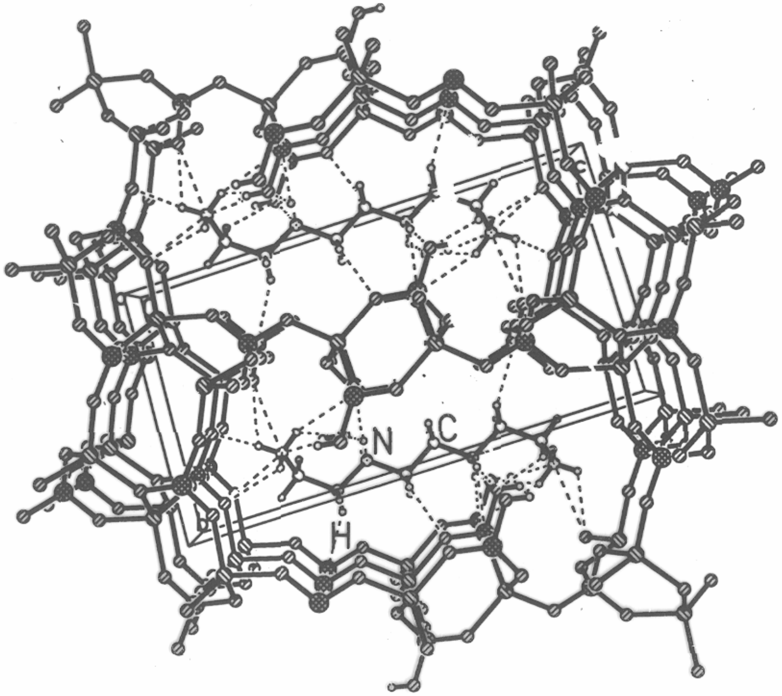
1D – Linear- chain



1D - Ladder

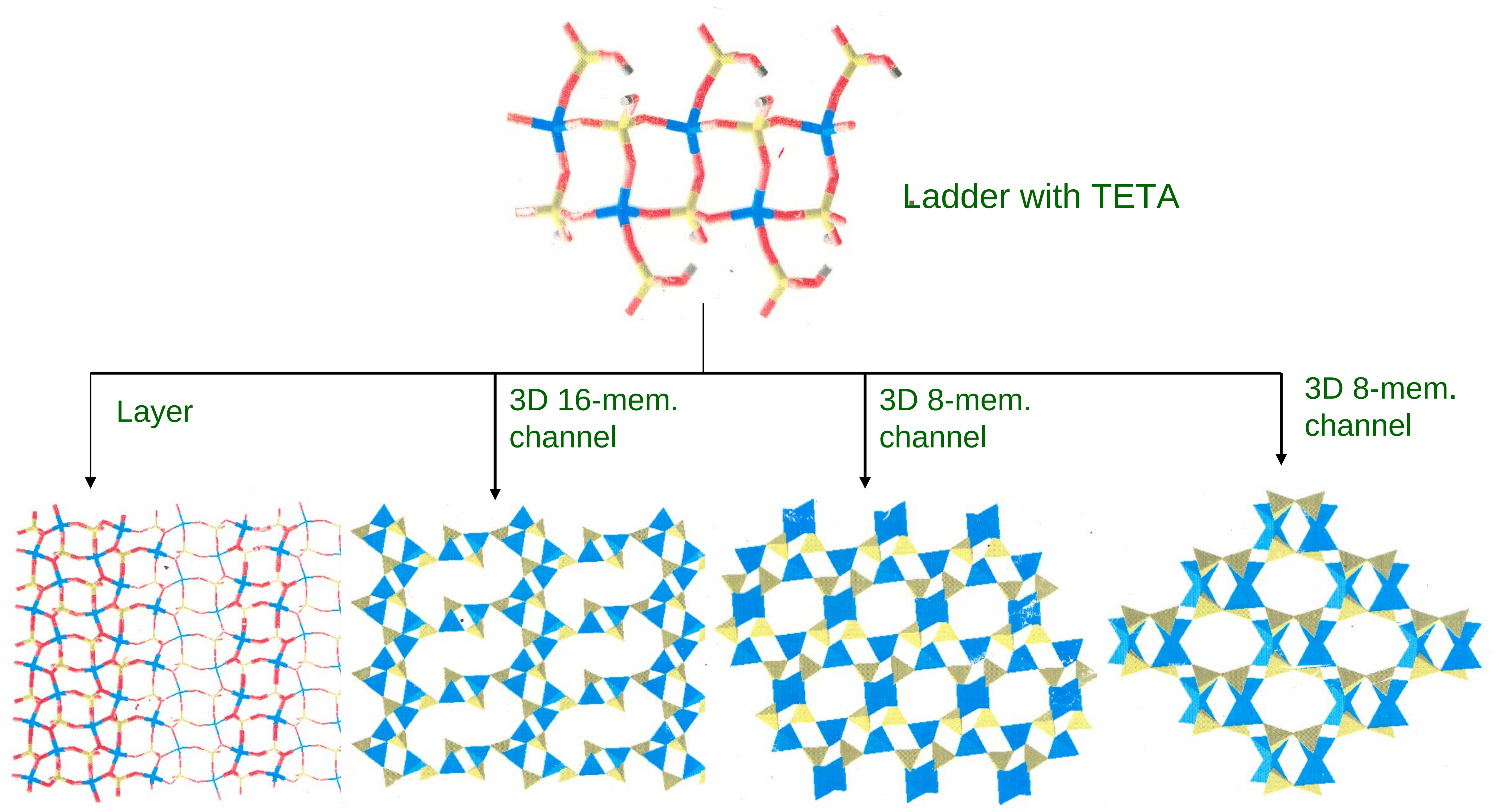


2D - layer



3D - channel

Transformations of a 1D-Ladder Zinc Phosphate to 2D and 3D Structures



Ladder with TETA

Layer

3D 16-mem. channel

3D 8-mem. channel

3D 8-mem. channel

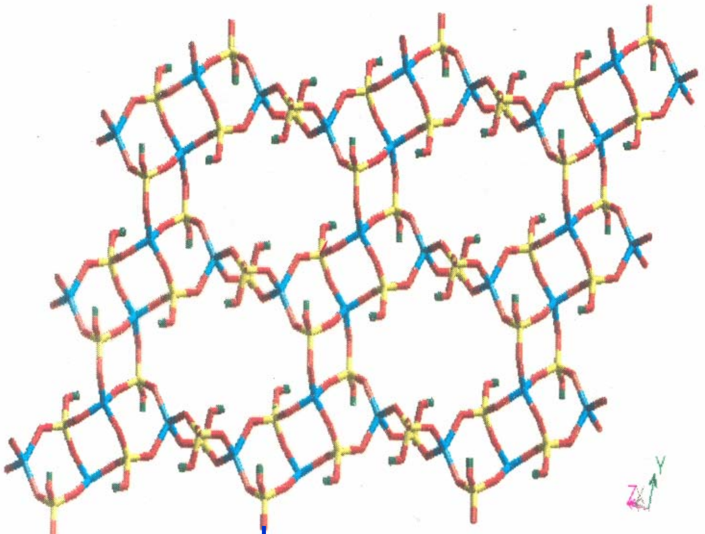
Rao et al *Acc. Chem. Res.*, 2000

Conditions of transformation

a: $A + TETA + H_2O \xrightarrow[24h]{150^0C} B$

b: $A + H_2O \xrightarrow[24h]{150^0C} C$

c: $A + Piperazine + H_2O \xrightarrow[72h]{110^0C} D + B$

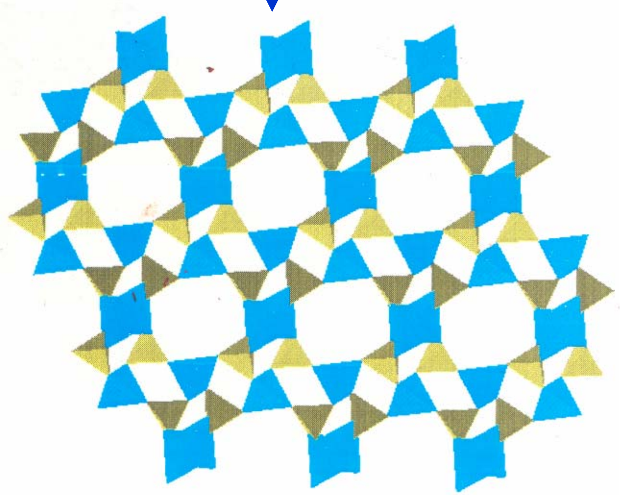


Layered $ZnPO_4$ with triethylene tetramine (TETA)
$[C_6N_4H_{22}]_{.5}[Zn_2(HPO_4)_3]$ **(A)**

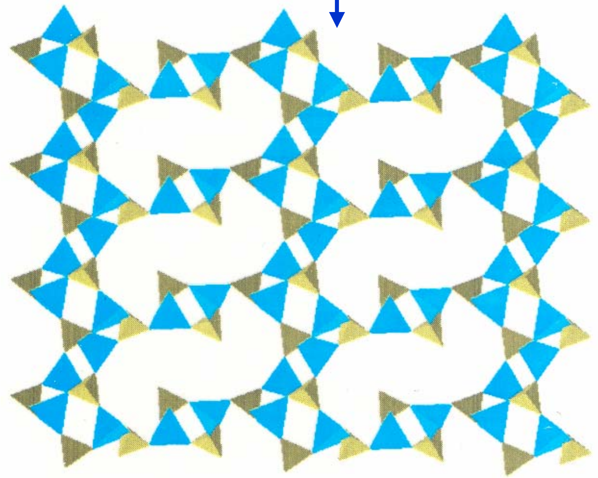
a

b

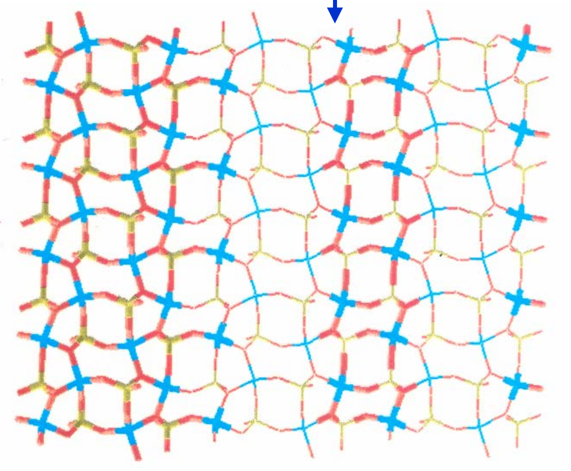
c



8-membered ring 3-D $ZnPO_4$
$[C_6N_4H_{22}]_{.5}[Zn_2(PO_4)_2]$ **(B)**

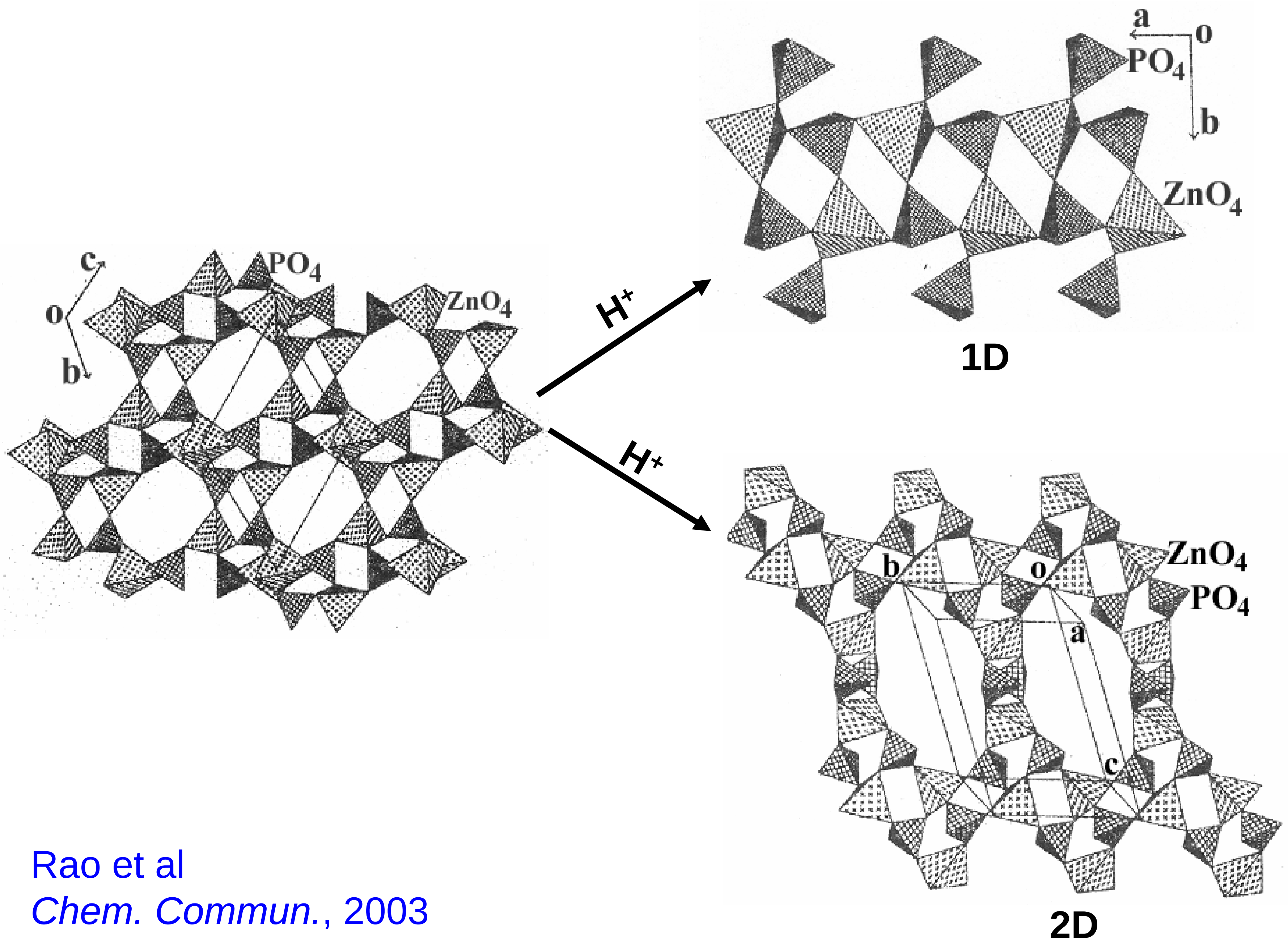


16-membered ring 3-D $ZnPO_4$
$[C_6N_4H_{22}]_{.5}[Zn_3(PO_4)_2(HPO4)]$ **(C)**

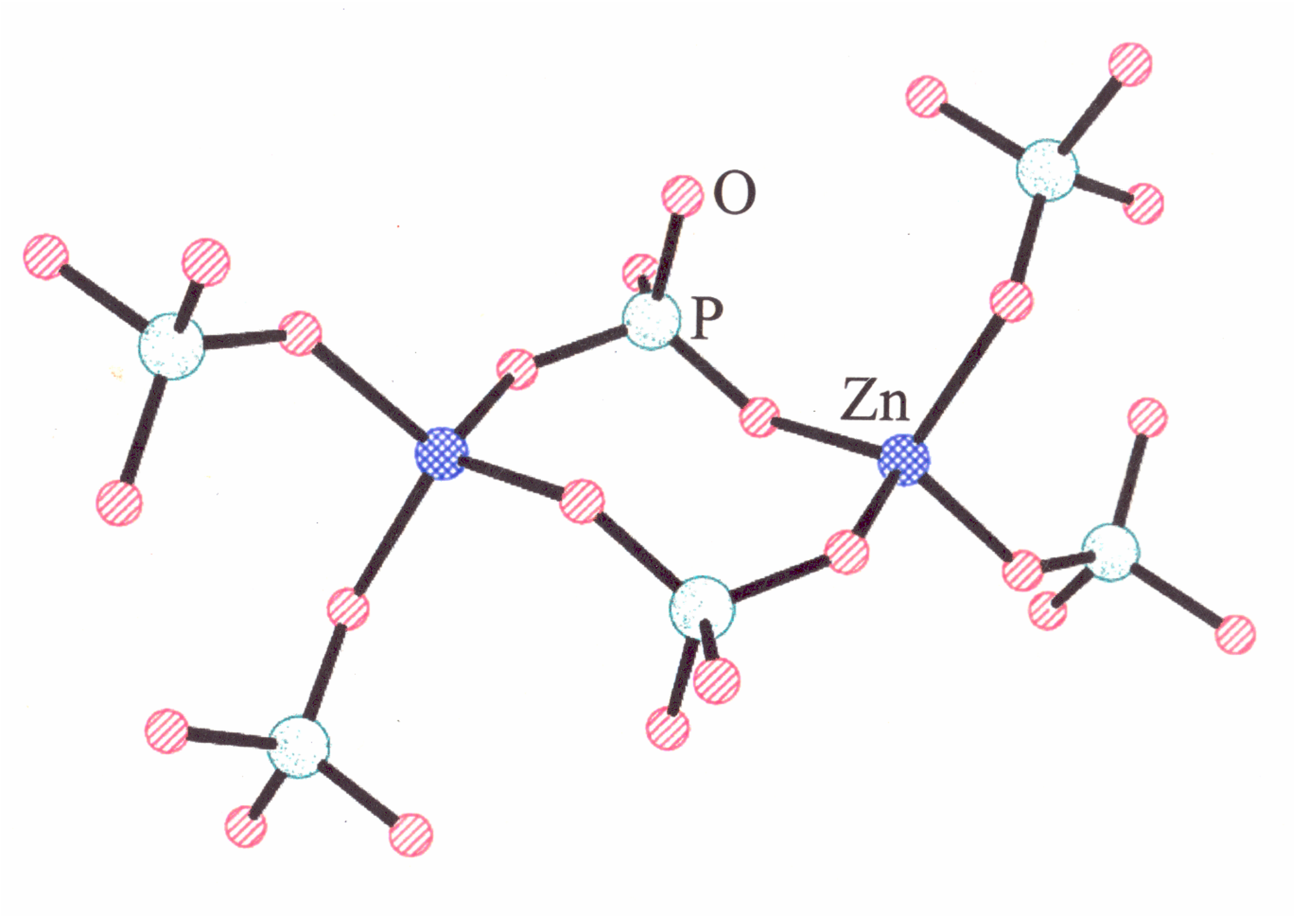


Layered $ZnPO_4$ + **(B)**
$[C_4N_2H_{12}][Zn_2(PO_4)_2]$ **(D)**

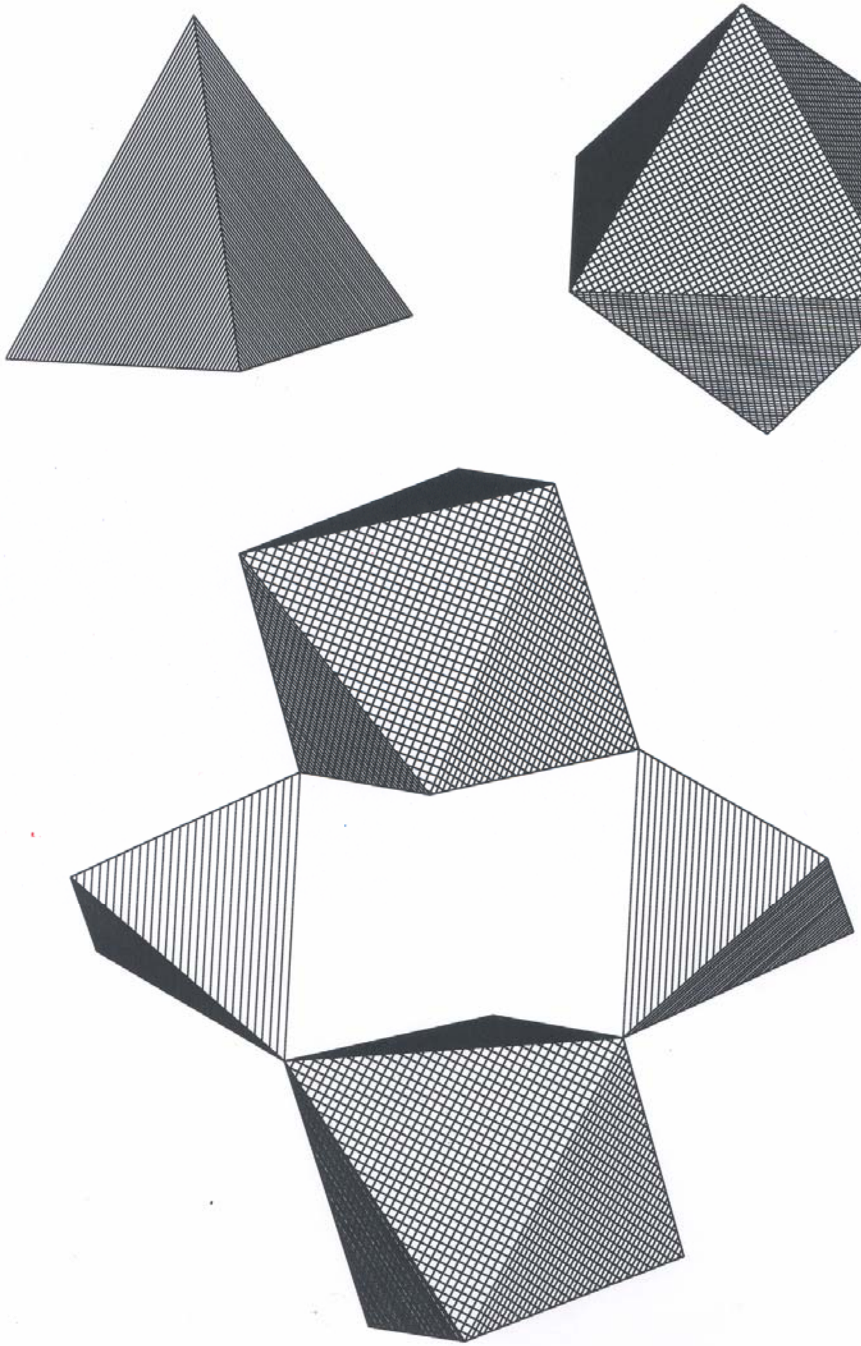
DEGRADATION STUDIES



Rao et al
Chem. Commun., 2003

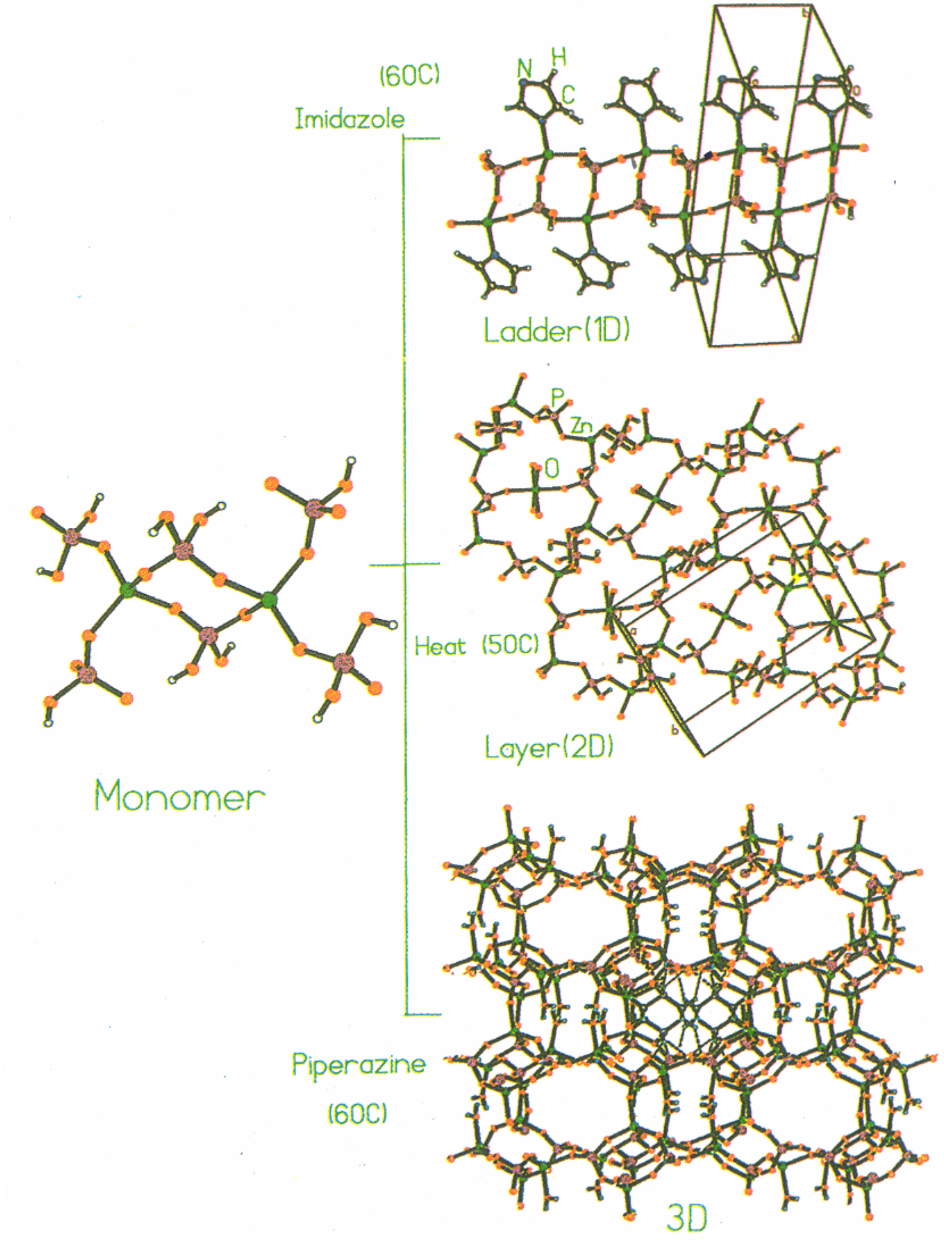


Zero dimensional Zinc Phosphate comprising a 4-membered ring



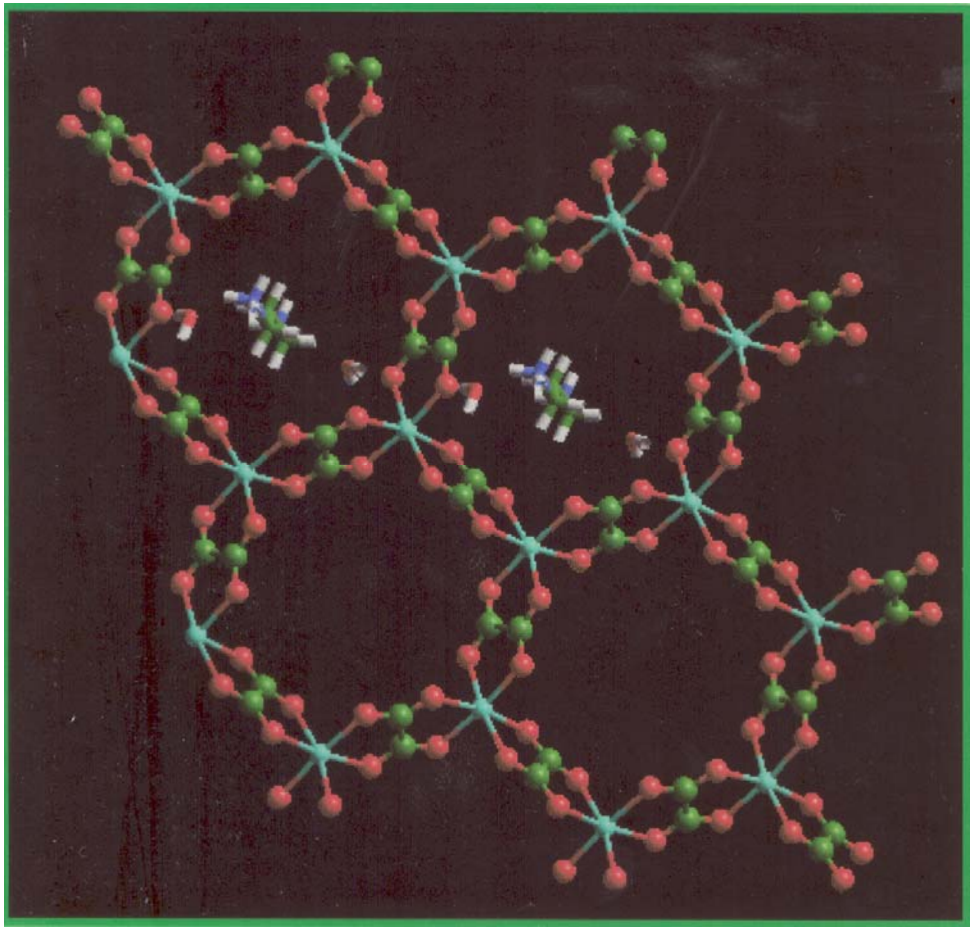
Secondary Building Units (SBU), Ferey

Transformations of a zero-dimensional monomeric zinc phosphate to 1D (ladder), 2D (layer) and 3D structures.



Neeraj, Choudhury & Rao, *J. Mater. Chem.*, 2002

Open-framework Metal Carboxylates

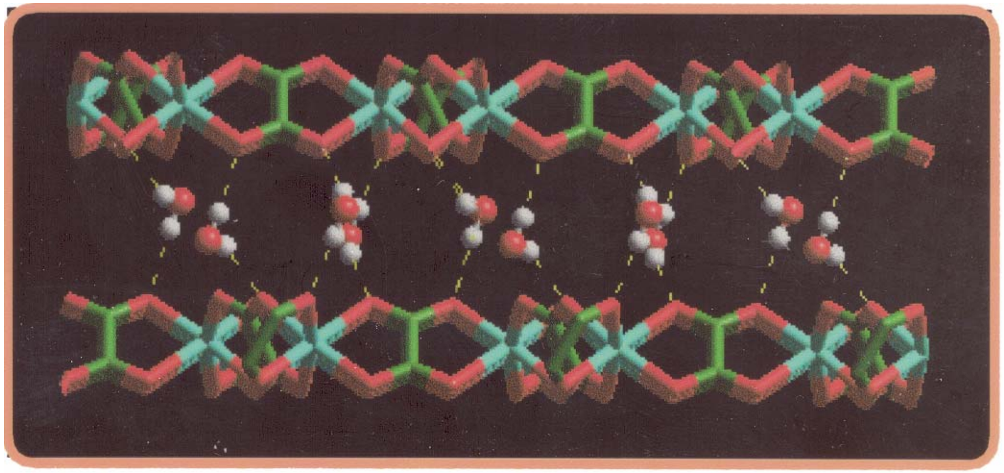


a = 9.261
b = 9.455
c = 12.487
α = 83.9
β = 88.0
γ = 61.1

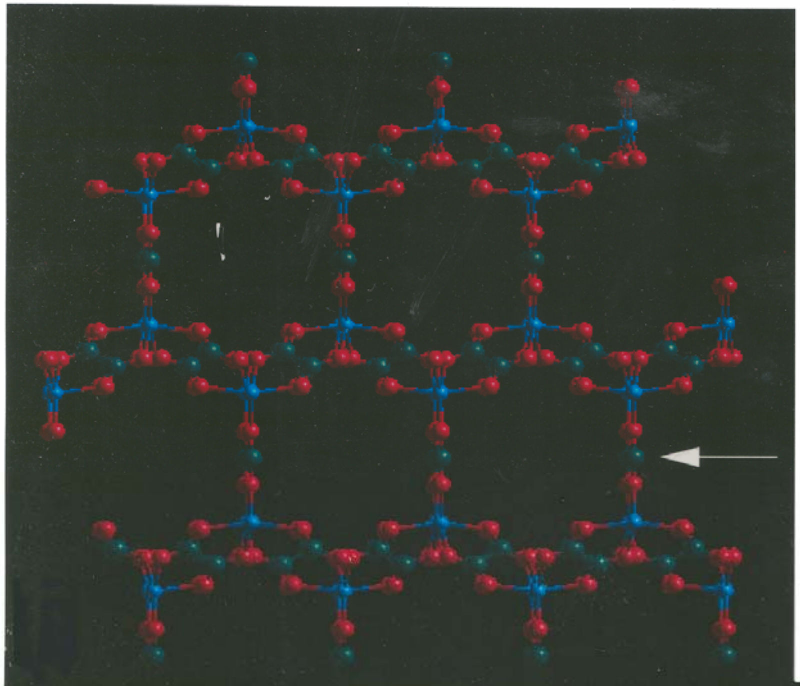
Honeycomb Architecture (Layer)
Amine and water molecules sit in the middle of the pores

Layer stabilized by extensive H-bonding by water molecules

$[C_3N_2H_{12}][Zn_2(C_2O_4)]$



Vaidhyanathan, Natarajan
Cheetham & Rao
Chem. Mater., 1999, 11, 3636



$[C_3NH_{10}][Zn_2(C_2O_4)_3]$

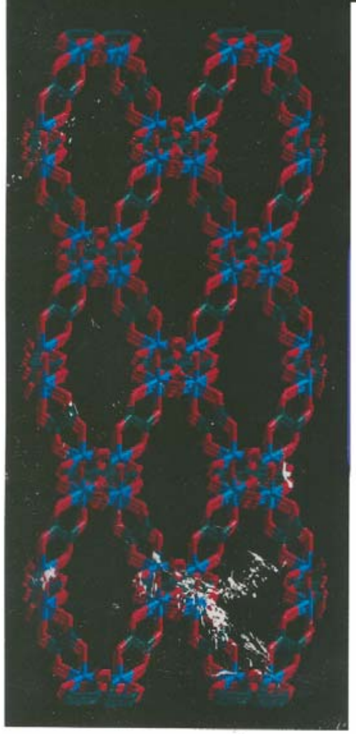
Three-dimensional Zinc Oxalate

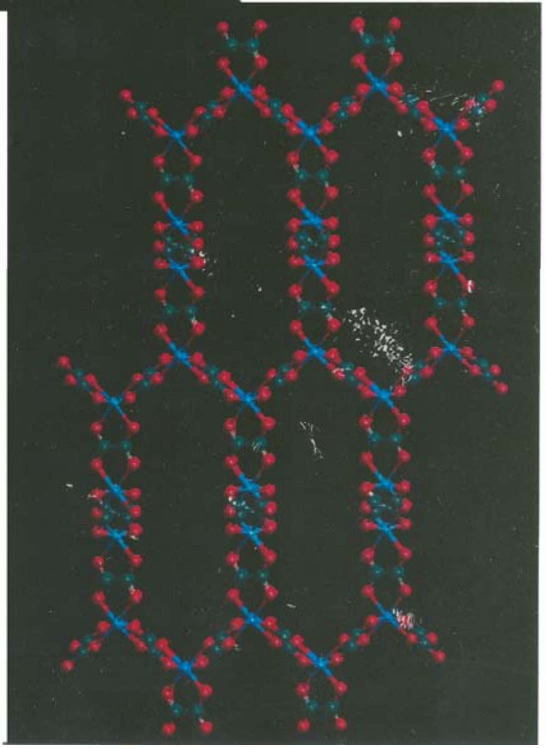
Arrow indicates ***out-of-plane*** Oxalate Units

Amine sits in the middle of the channel

Max. dia:7 ang.

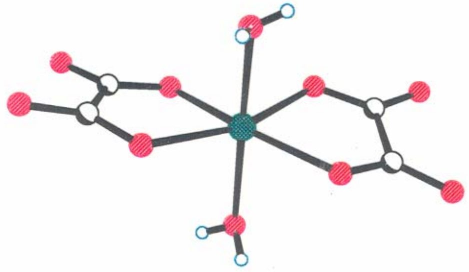
a = 15.847
b = 9.685
c = 18.333
β = 115.5

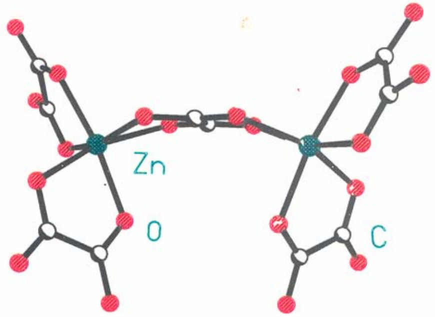




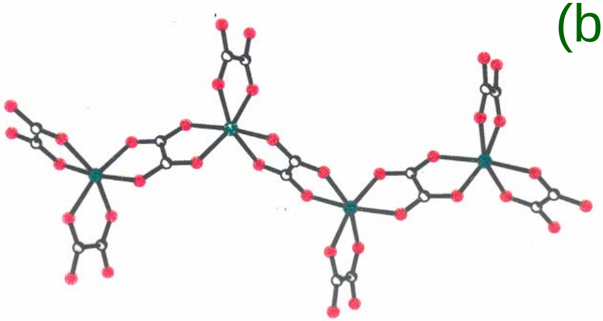
Vaidhyanathan, Natarajan Cheetham & Rao *Chem. Mater.*, 1999, 11, 3636

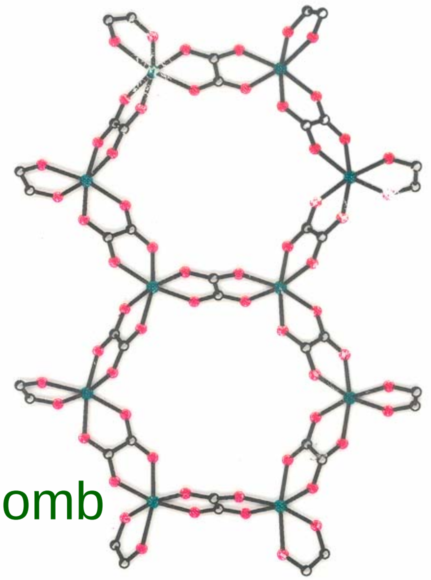
HIERARCHY OF ZINC OXALATES:
O-, I-, 2-, & 3D
(FROM AMINE OXALATES)

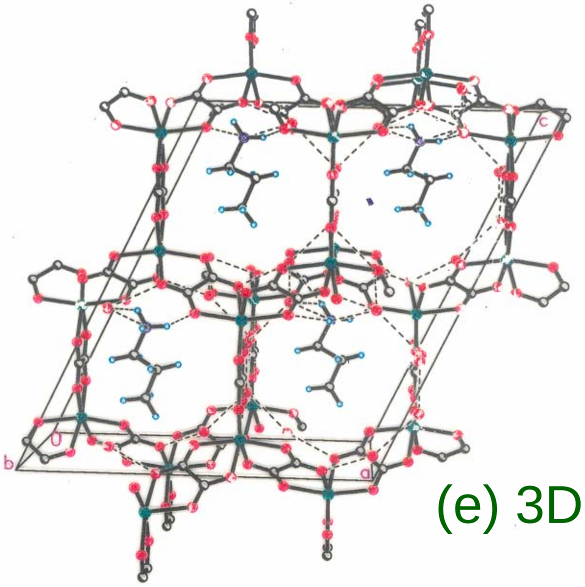

(a) Monomer



(b) Dimer

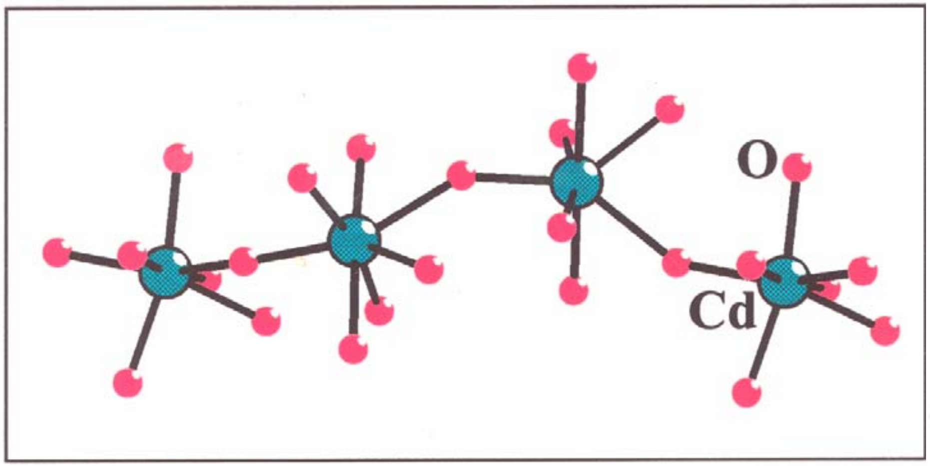

(c) Chain

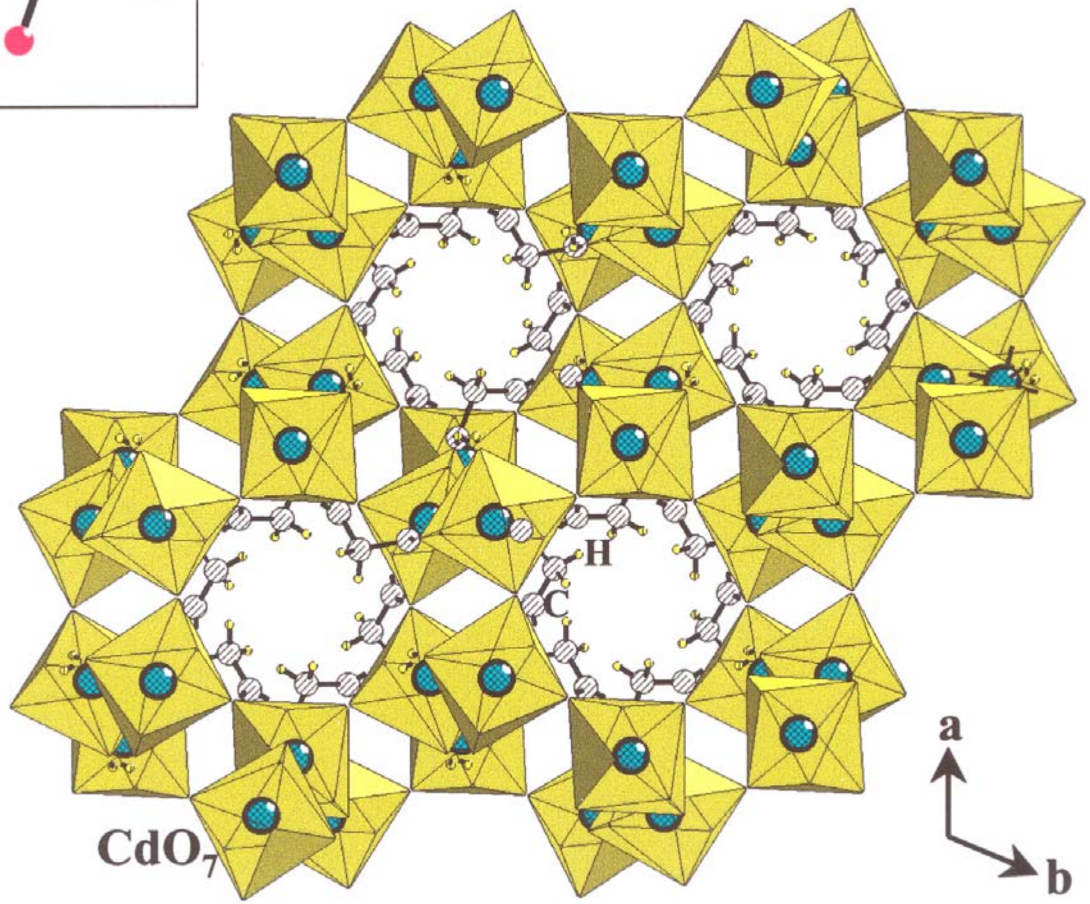

(d) 2D Honeycomb



(e) 3D (channel)

Rao et al *Acta Cryst* (Review) 2000
Vaidhyanathan, Natarajan & Rao *Dalton Trans.*, 2001





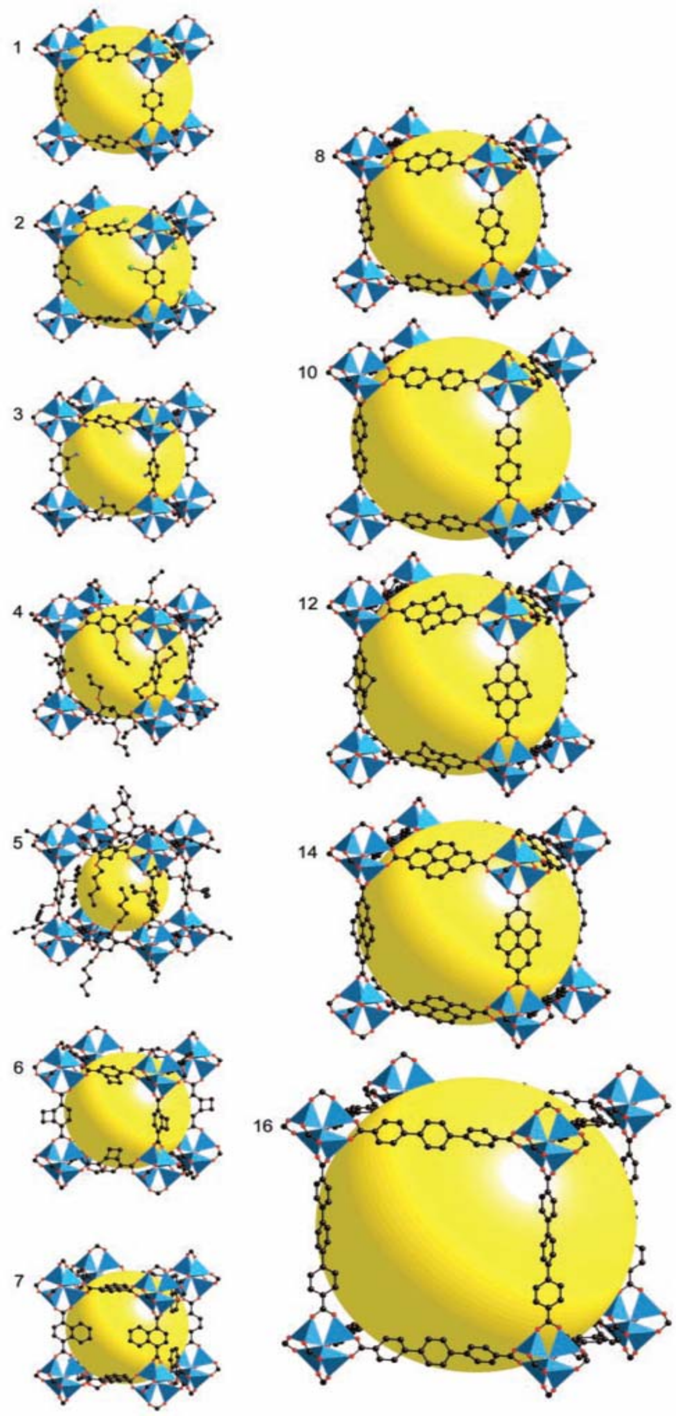
Vaidhyanathan,
Natarajan & Rao
Dalton Trans.,
2003, 8, 1459

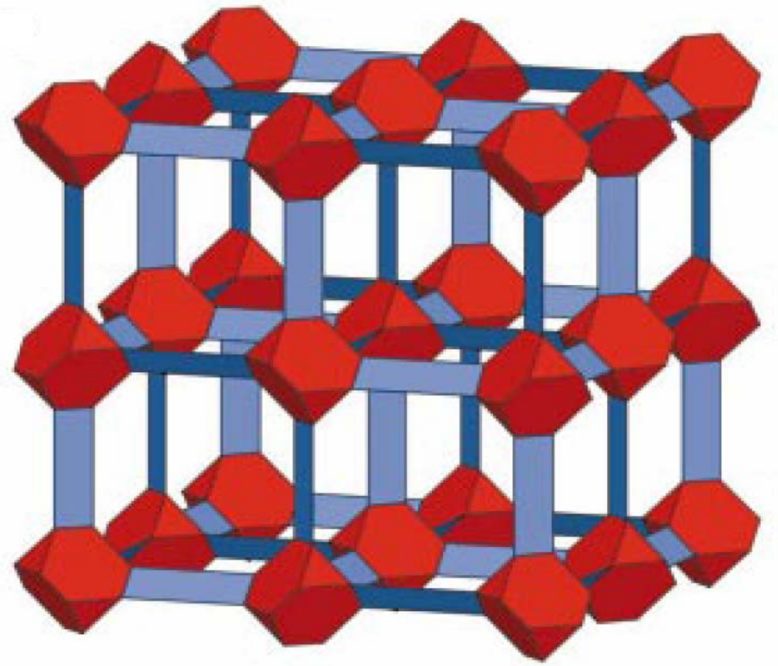
CARBOXYLATES

are good components for designing
novel open-framework structures,
coordination polymers and porous solids

See: C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew Chem. Int. Ed*., 2004, 43(12), 1466

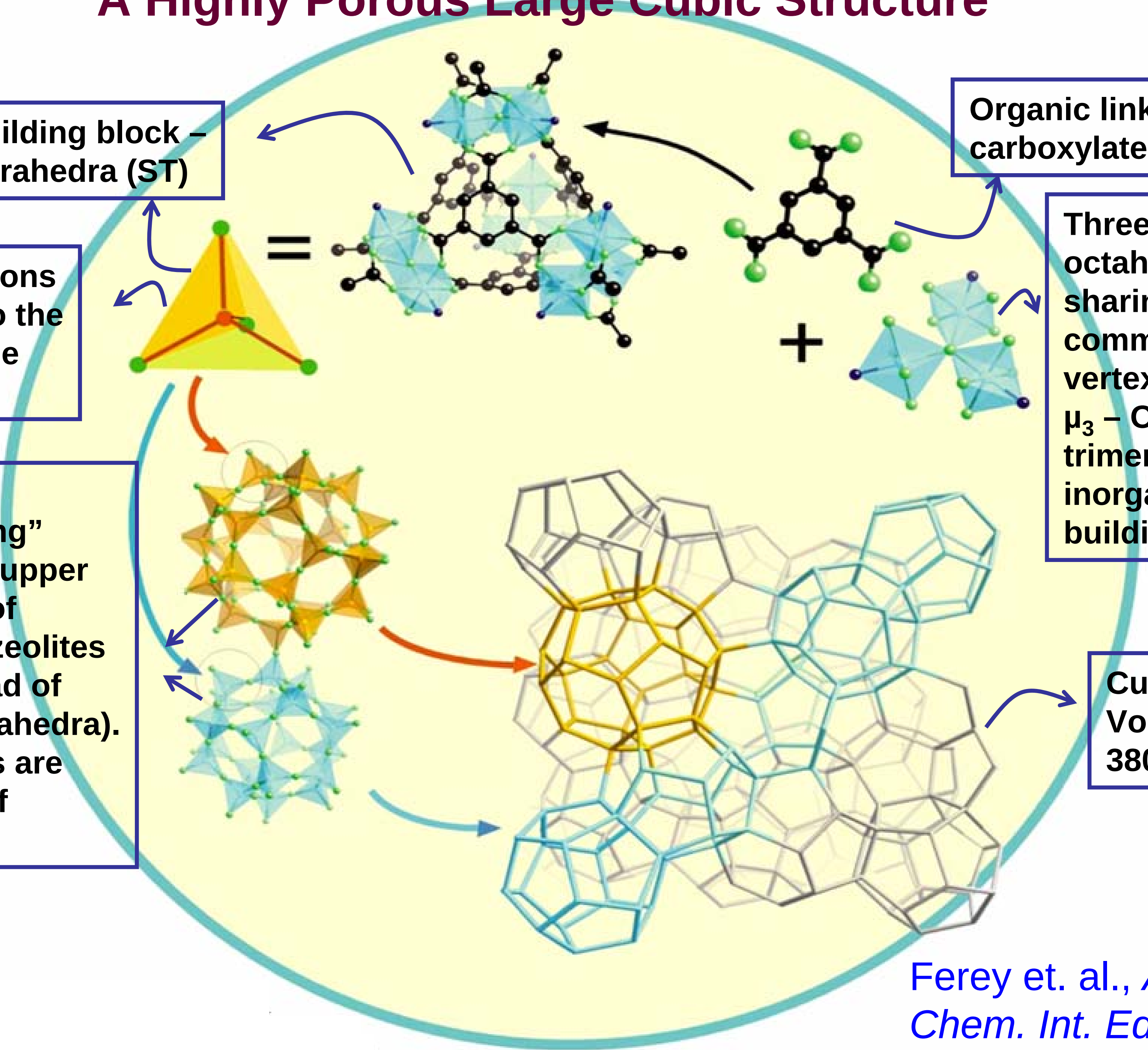
Isoreticular series of MOFs based on α-Po net structure





Yaghi et. al.,
Science 2002, 295, 469

A Highly Porous Large Cubic Structure



Hybrid building block – Super Tetrahedra (ST)

Organic linker with carboxylate groups

Cage dimensions correspond to the domains of the micropores

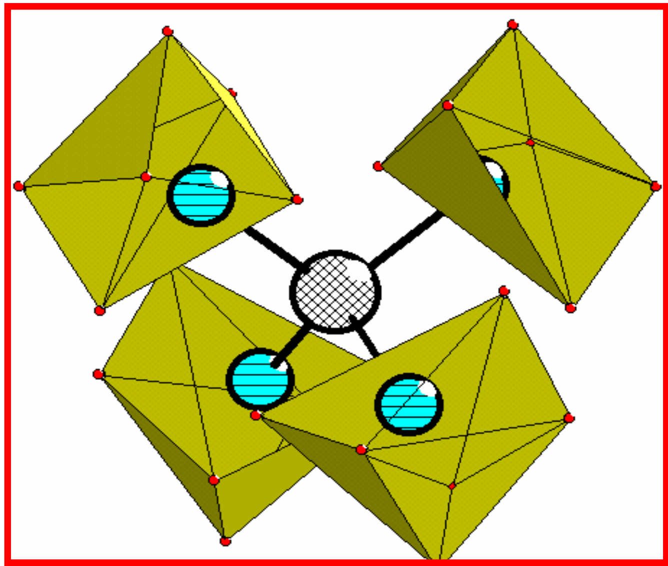
Three octahedra sharing a common vertex μ_3 – O ⟶ trimeric inorganic building block

3D network of "corner sharing" ST (similar to upper homologues of silicates and zeolites with ST instead of small TO_4 tetrahedra). Cage domains are in the range of mesopores

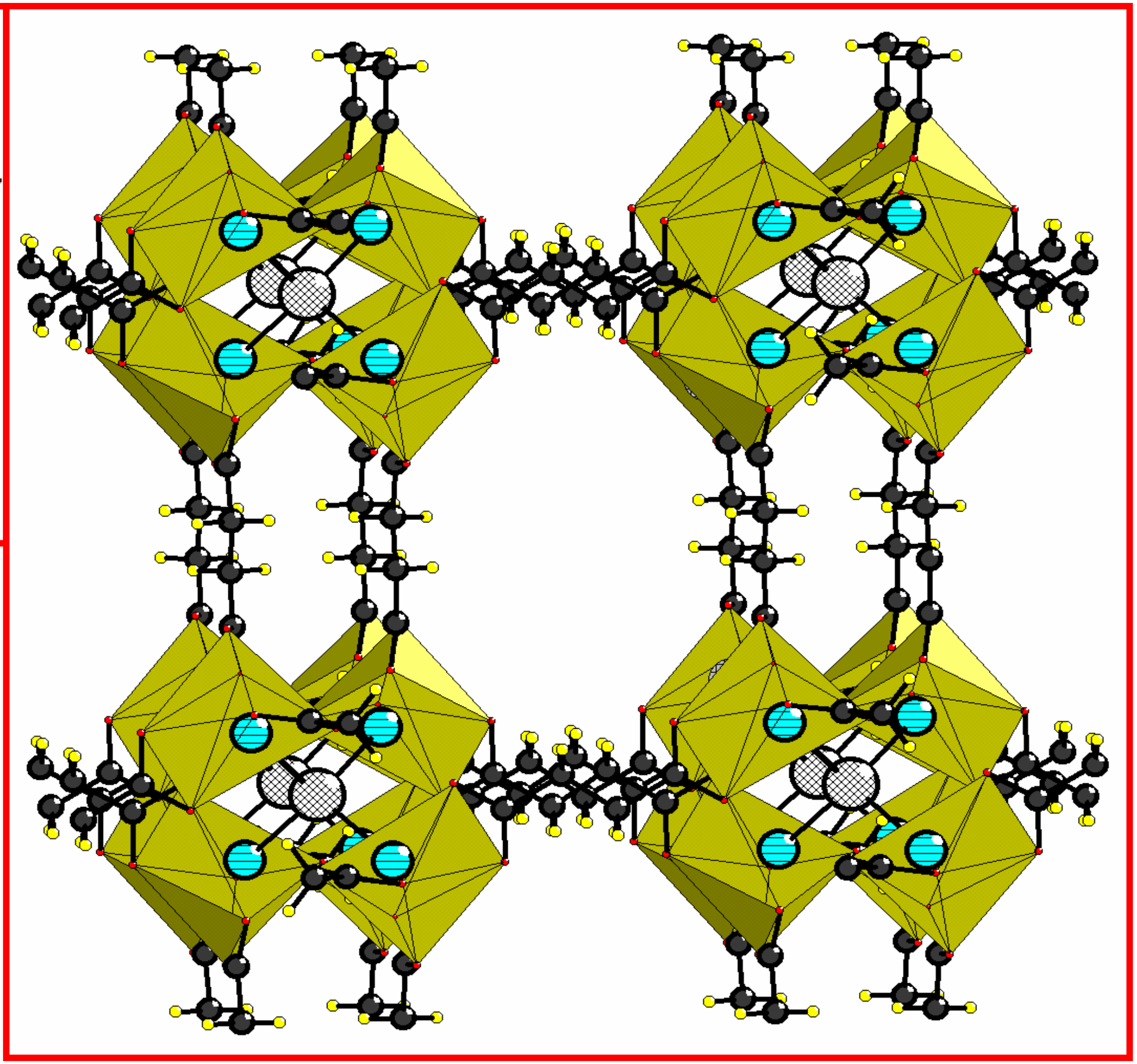
Cubic cell Volume ~ 380 000 Å^3

Ferey et. al., *Angew Chem. Int. Ed.*, 2004

Three-Dimensional Cadmium Succinate, $[Na_3Cd_5(C_4H_4O_4)_6X]$ (X =Cl, Br) -XCd_4O_{24} Tetrahedral Clusters



Inset: XCd_4O_{24} cluster (X =Cl, Br)



▨ **- Cl or Br**

● **- Cd**

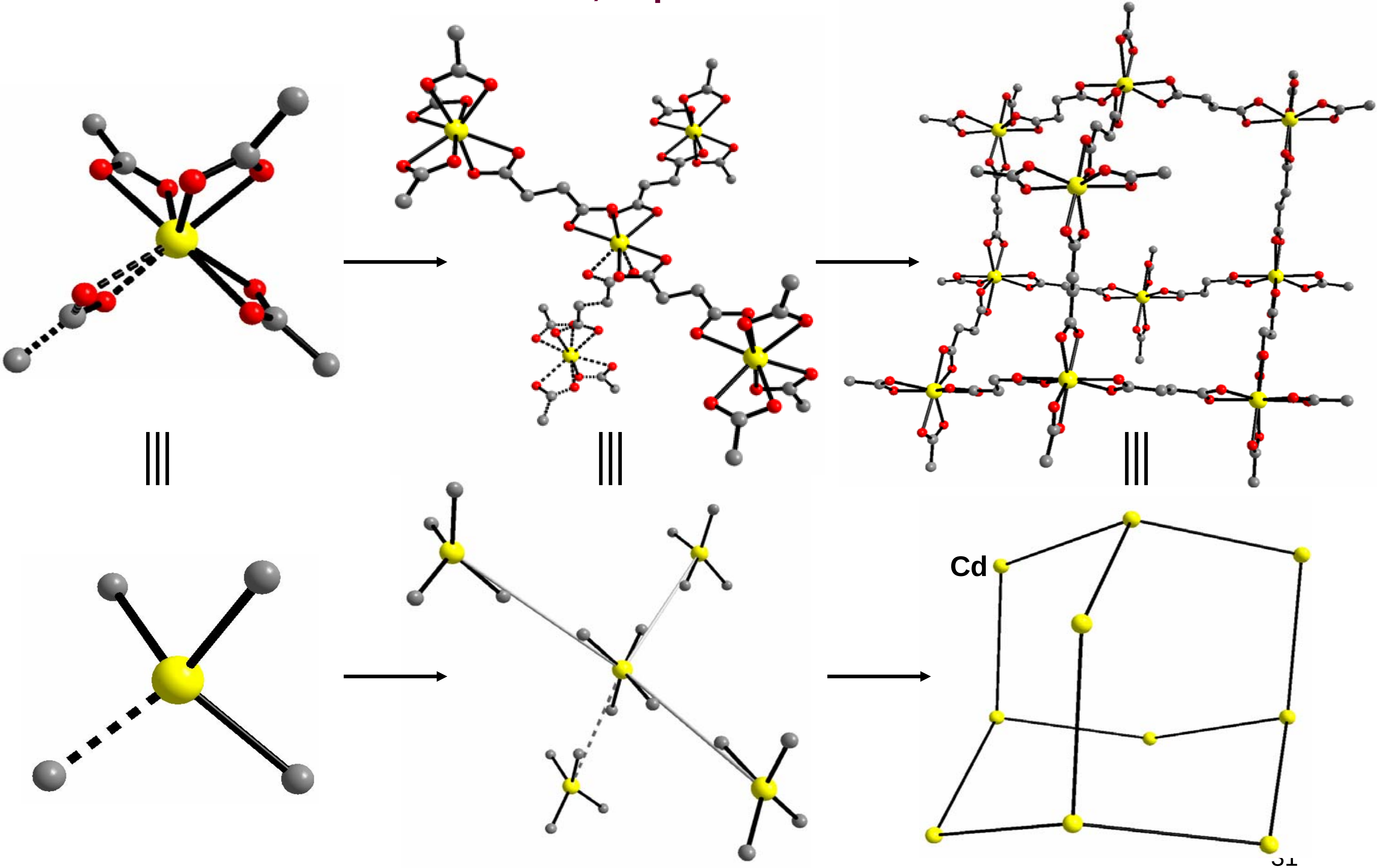
● **- O**

● **- C**

● **- H**

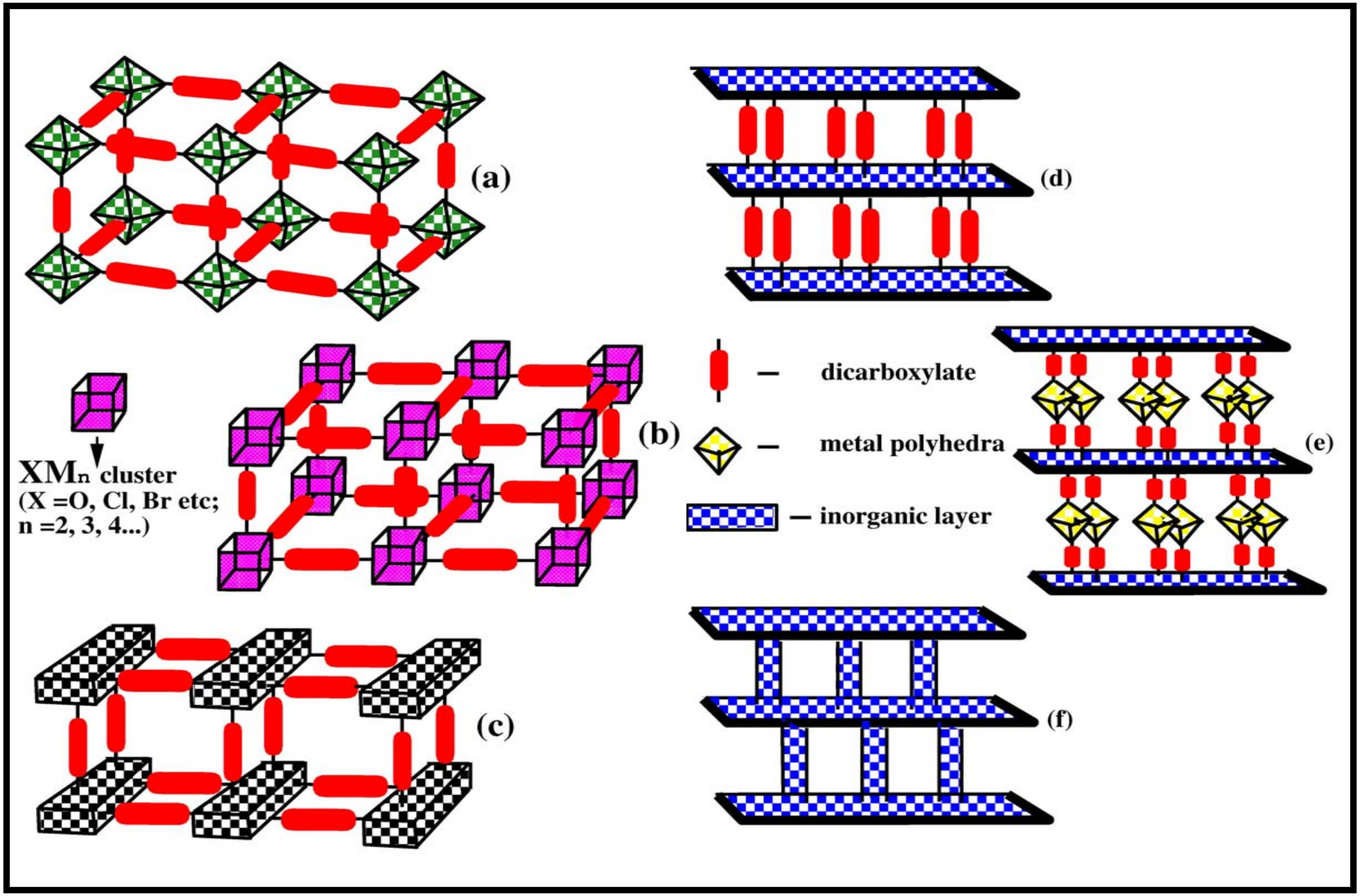
Vaidhyanathan, Natarajan & Rao, *Crystal Growth and Design*, 2003, 3, 47

Cadmium Succinate tetrahedron, supertetrahedron and the adamantane unit



Vaidhyanathan, Natarajan, Rao, *Inorg. Chem.*, 2002, 41, 5226

Design of Three-dimensional Structures from "Predetermined" Building Units

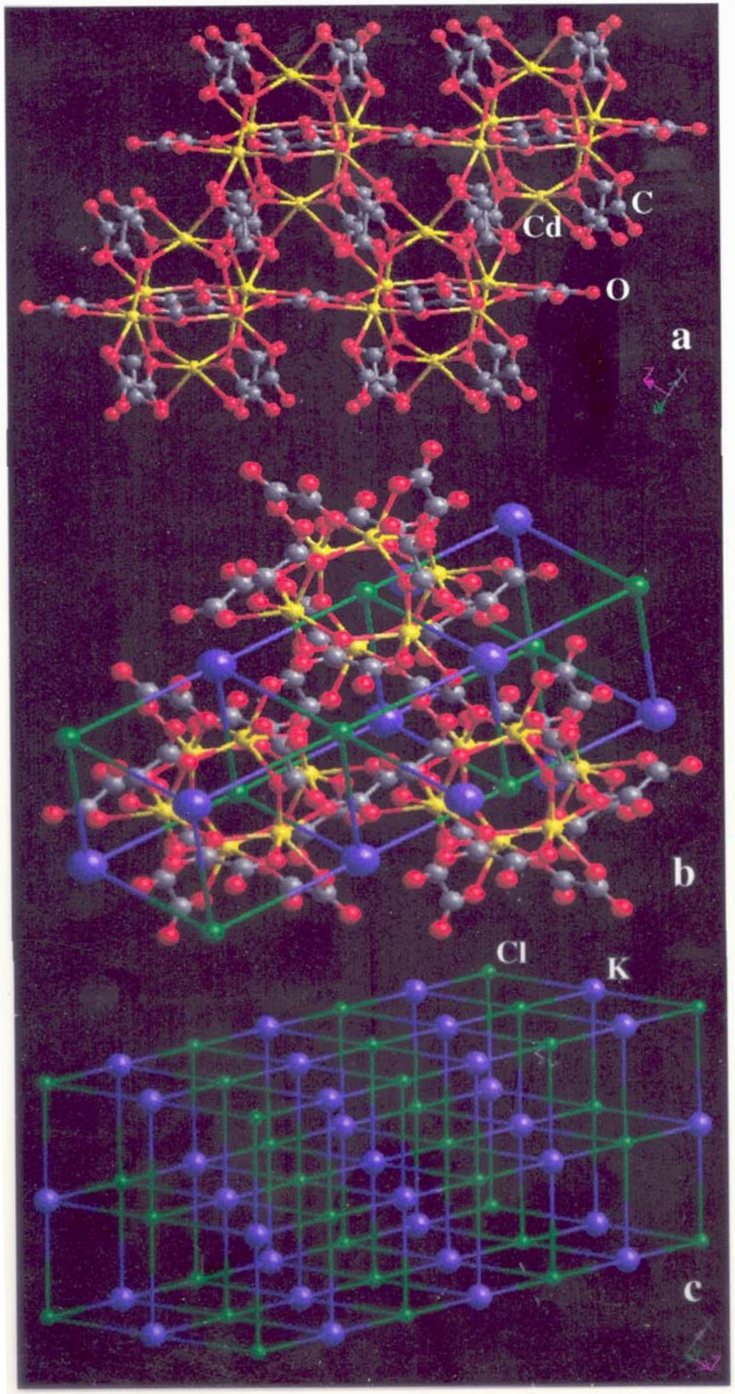


C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew Chem. Int. Ed.*, 2004, 43(12), 1466

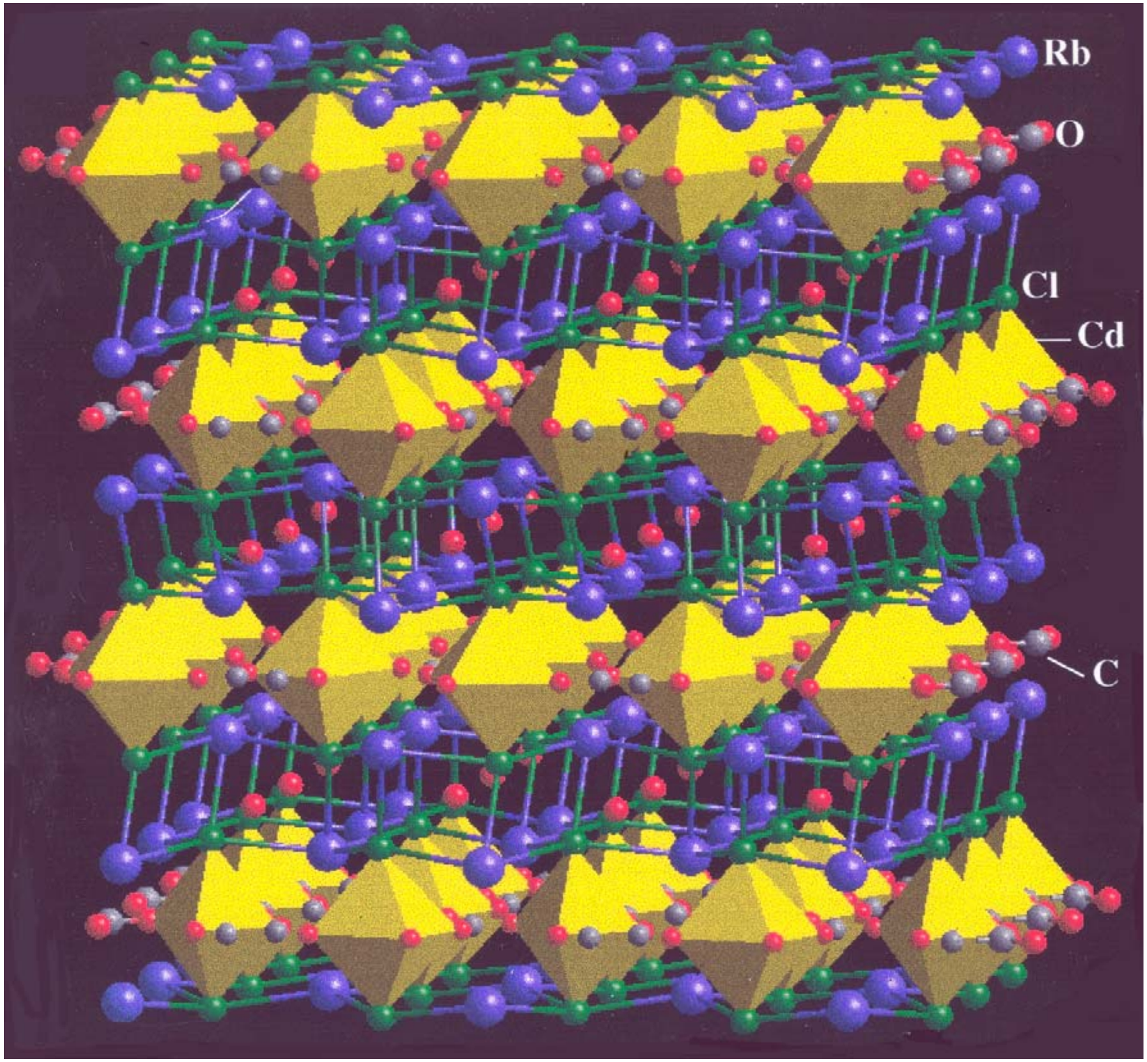
A simple reaction

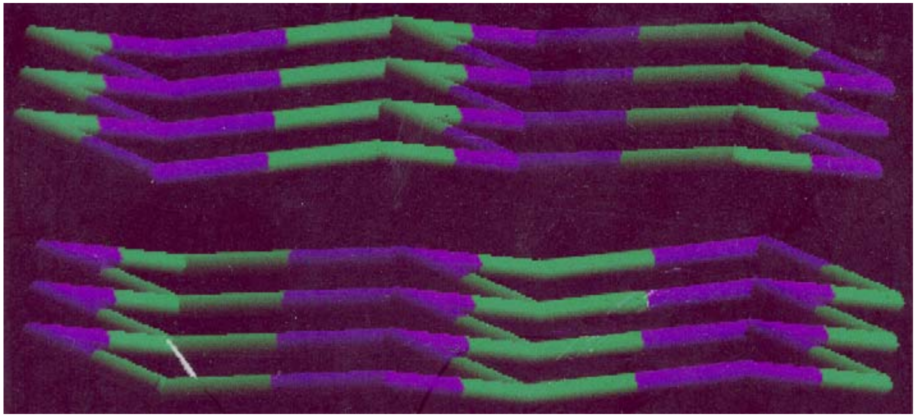
$CdCl_2$ + Na oxalate $\longrightarrow$ Cd oxalate + NaCl

But becomes fascinating if the reaction is carried out under solvo / hydrothermal conditions.



Vaidhyanathan,
Natarajan
Rao et al
Angew. Chem.,
2000,





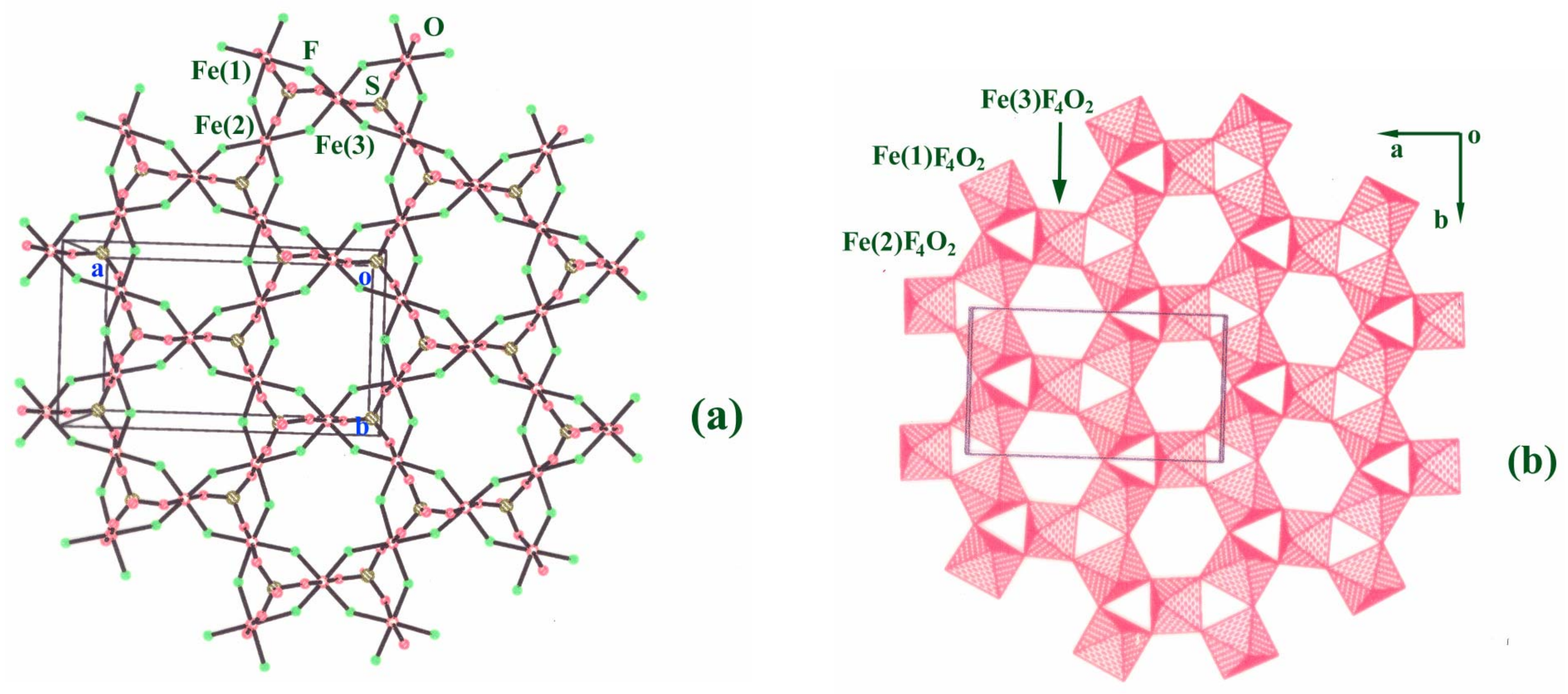
Br – Purple,
Cs - Green

Why only Phosphates or Silicates?

Can we use other oxyanions to build open-framework structures?

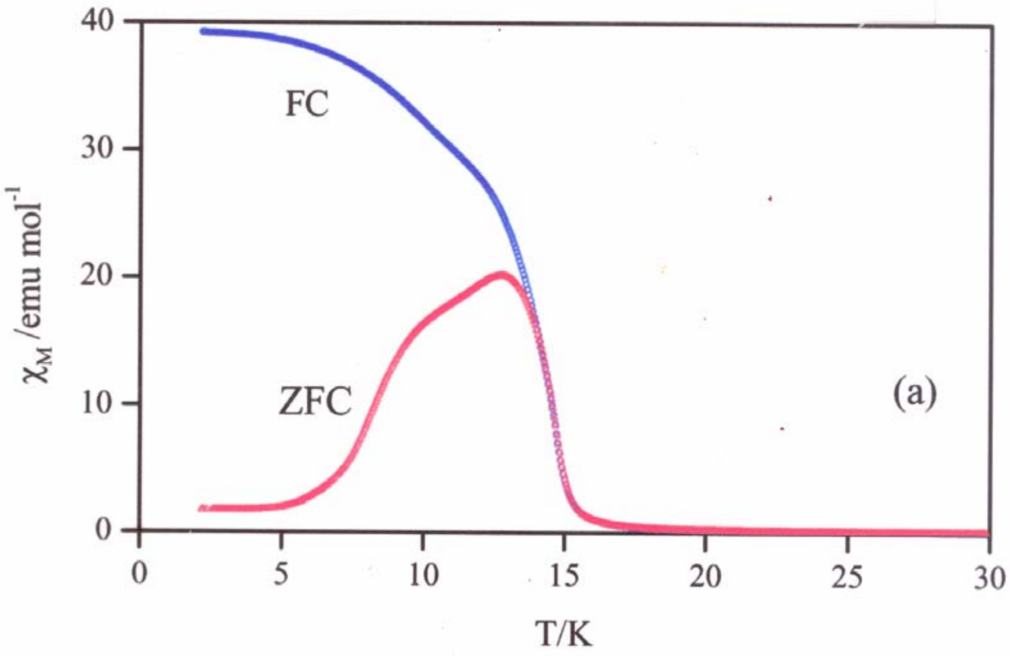
Sulfate, Selenate, Selenite

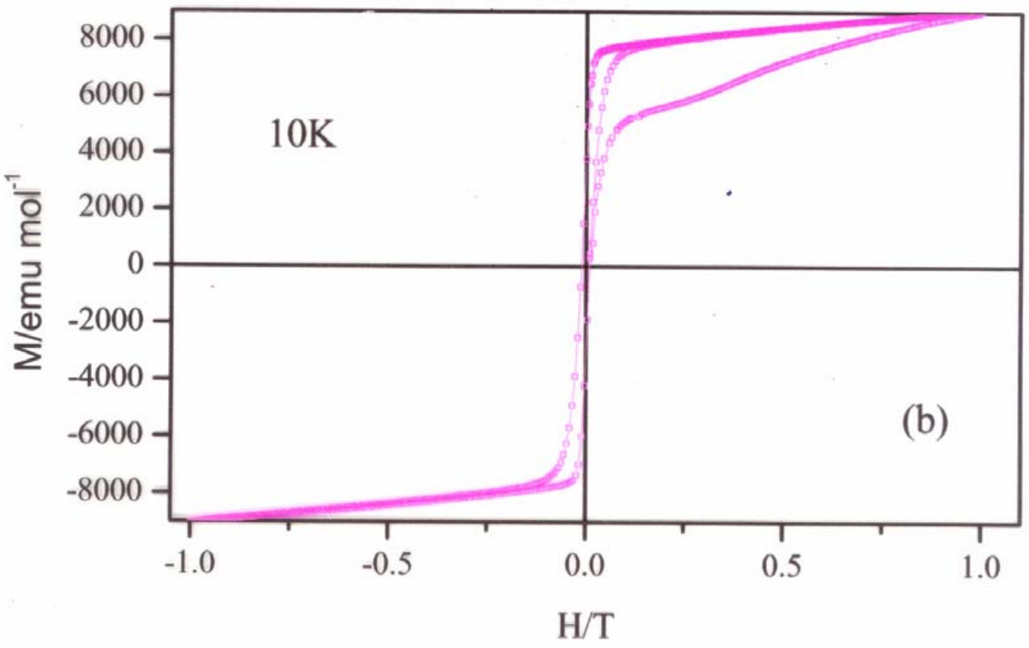
USE OF OTHER ANIONS



Fe(II)Fe(III) Sulfate

Rao et. al.
Angew. Chem. 2002


FC
ZFC
(a)
χ_M /emu mol^{-1}
T/K
0
10
20
30
40
0
5
10
15
20
25
30

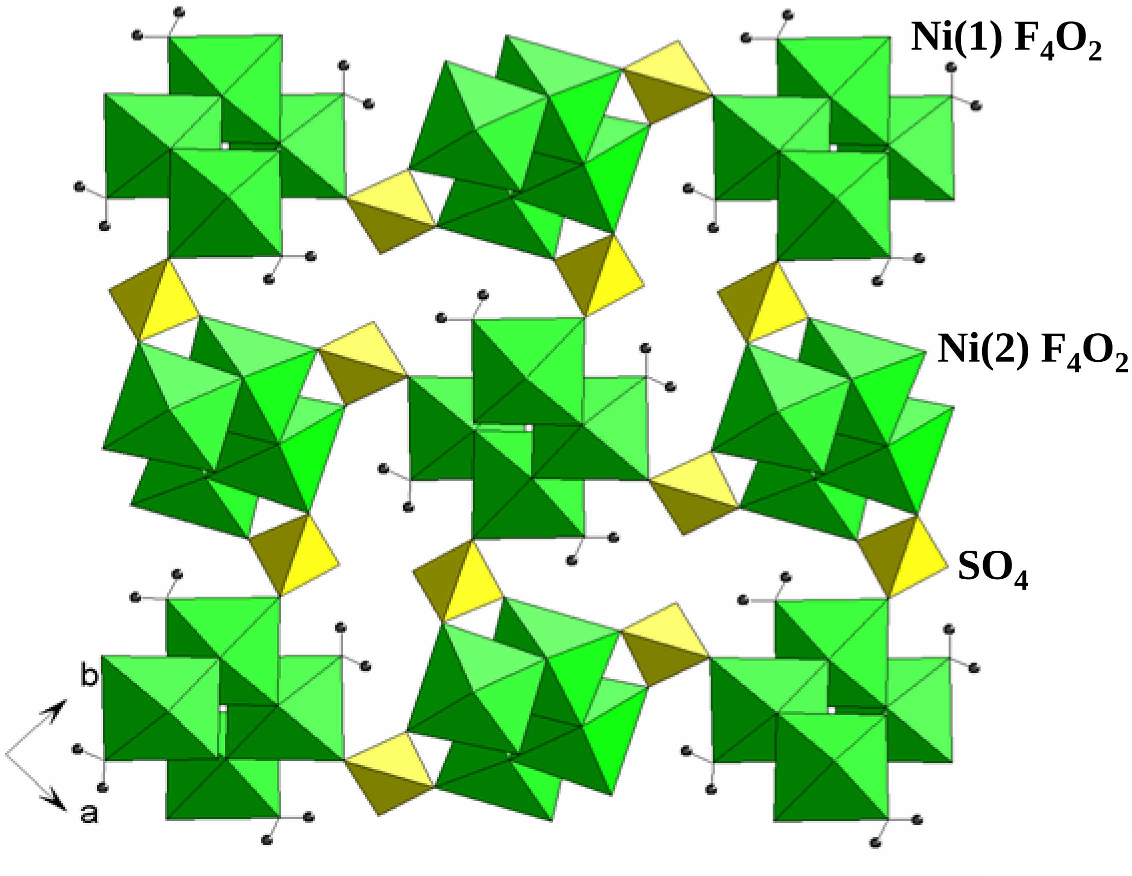

10K
(b)
M/emu mol^{-1}
H/T
8000
6000
4000
2000
0
-2000
-4000
-6000
-8000
-1.0
-0.5
0.0
0.5
1.0

Unusual Magnetic Properties of Kagome Structures

Fe^{3+}	Frustration, AFM
Fe^{2+}, Fe^{3+}	Ferrimagnetic (Low Temp)
Fe^{2+}	Ferrimagnetic (Low Temp)
Co^{2+}	Frustration, AFM
V^{3+}	Ferri/Ferromagnetic (Low T)

Fe^{3+} (S = 5/2), Co^{2+} (S = 3/2), Cr^{3+} (S = 3/2)
Fe^{2+} (S = 2), V^{3+} (S = 1)

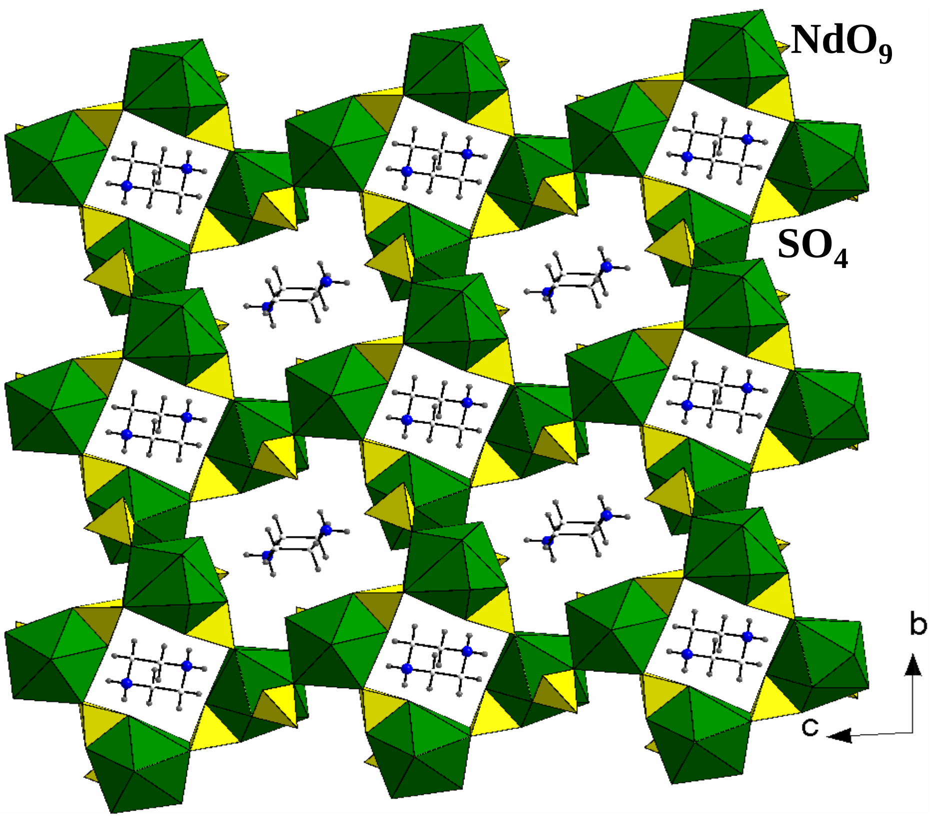
Three-dimensional Ni(II) sulfate



$[C_4N_2H_{12}][Ni_3F_4(SO_4)(H_2O)]$

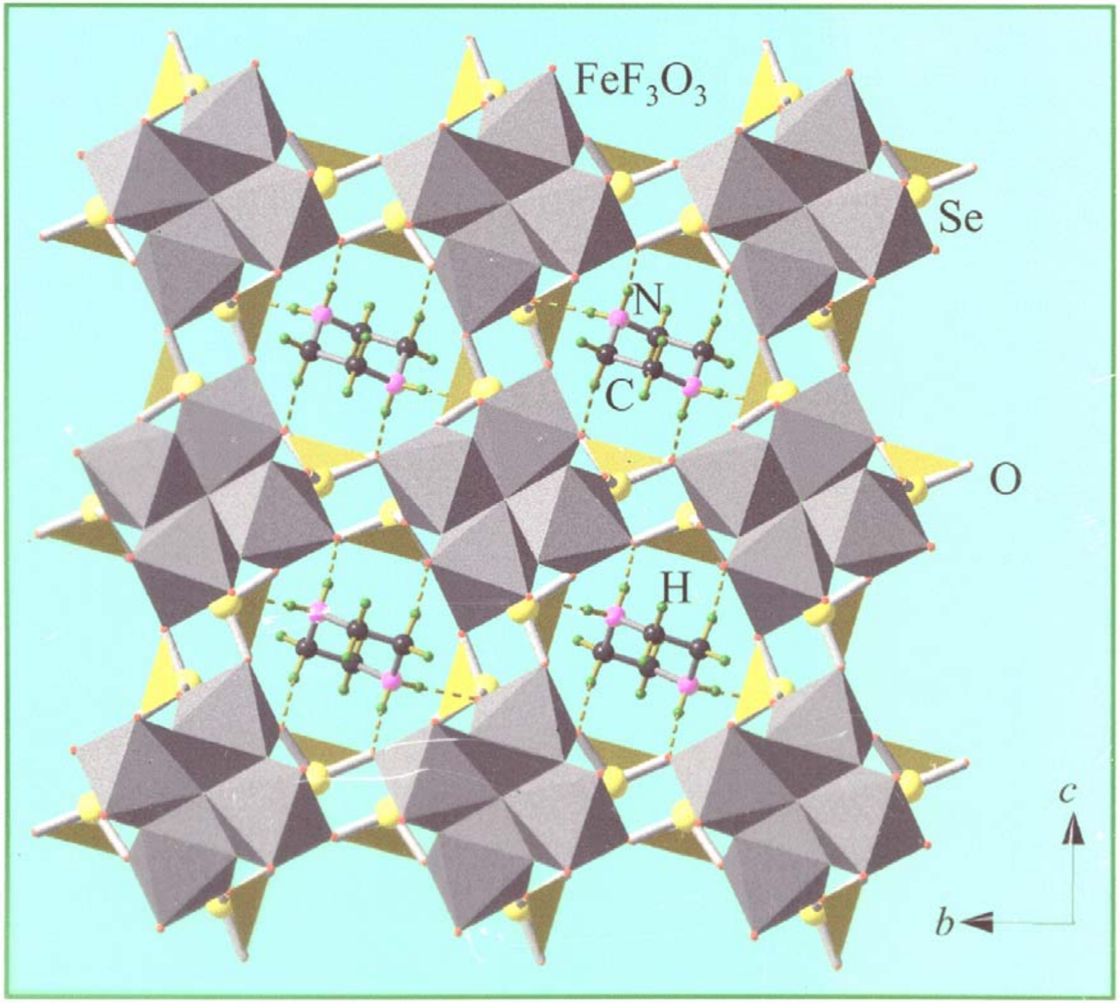
J. N. Behera and C. N. R. Rao
Inorg. Chem., 2004, 43, 2636

Three-dimensional neodymium sulfate



$[C_4N_2H_{12}][Nd_2(SO_4)_4(H_2O)_2]$

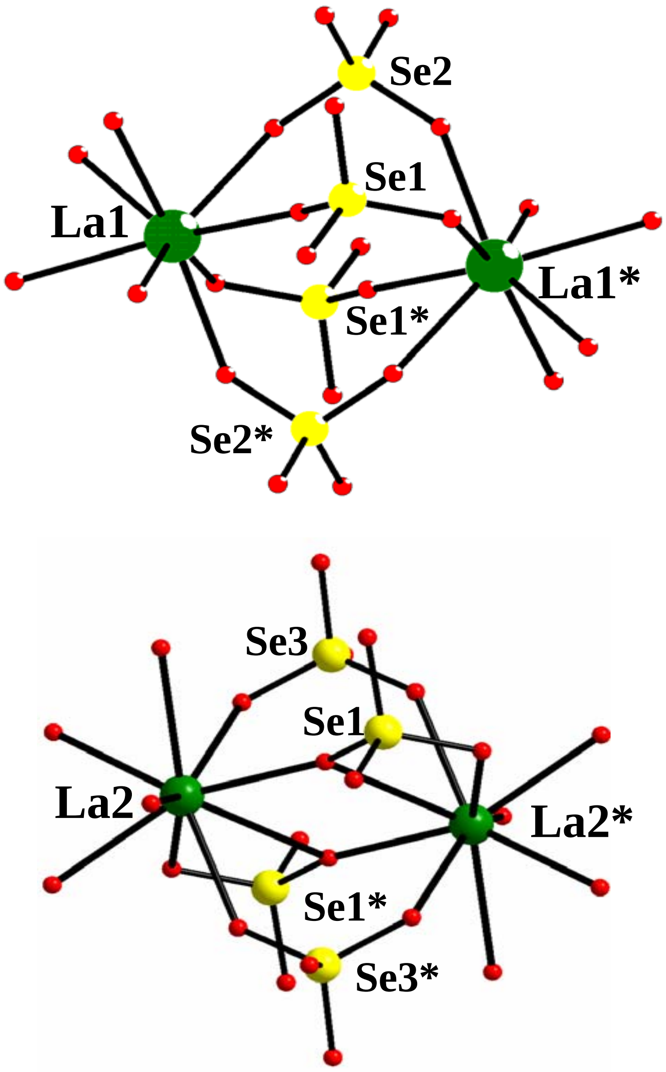
Dan, Behera, C. N. R. Rao
J. Mater. Chem., 2004, 14, 1257



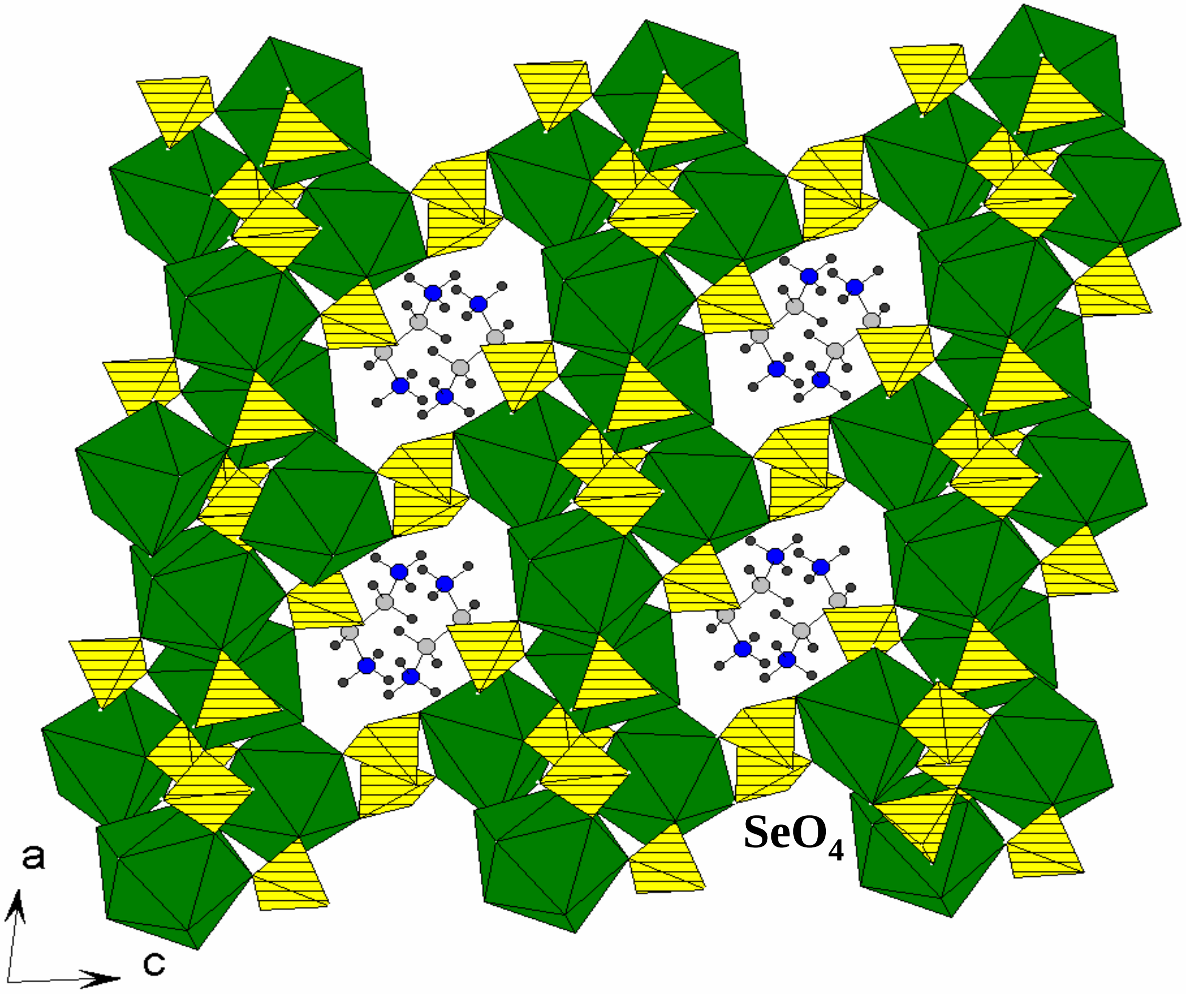
Polyhedral view of the inorganic framework of $[C_4N_2H_{12}]_{0.5}[Fe_2F_3(SeO_3)_2]$ along the b-axis showing 1D 8-membered channel. The protonated amine molecules are located inside the channels and forms N-H…O hydrogen bonds with the framework (dotted lines)

A.Choudhury & Rao
Angew. Chem., 2001

Three-dimensional Lanthanum Selenate



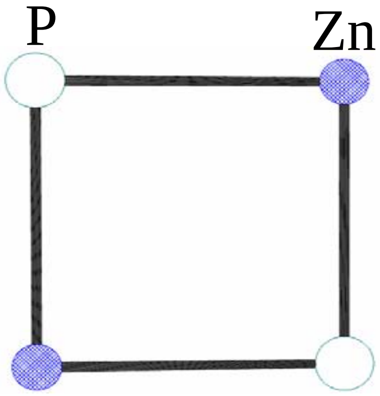
La_2Se_4 building units



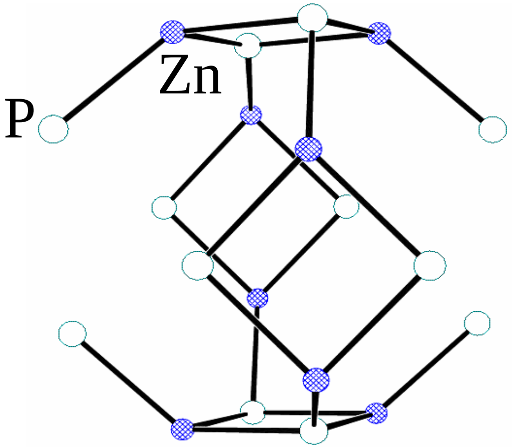
$[C_2N_2H_{10}][La_2(SeO_4)_4(H_2O)_3].H_2O$

Behera & Rao
Chem. Commun., 2004

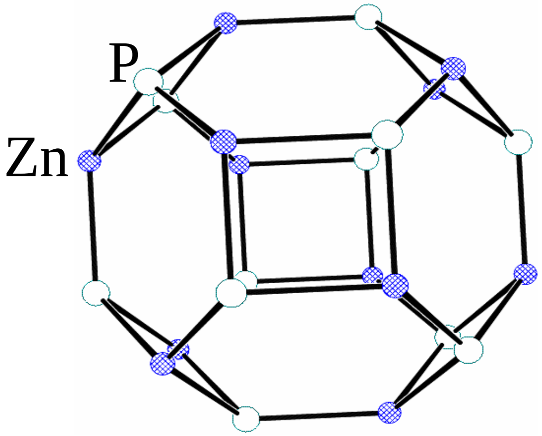
MOLECULE → MATERIAL
TRANSFORMATIONS



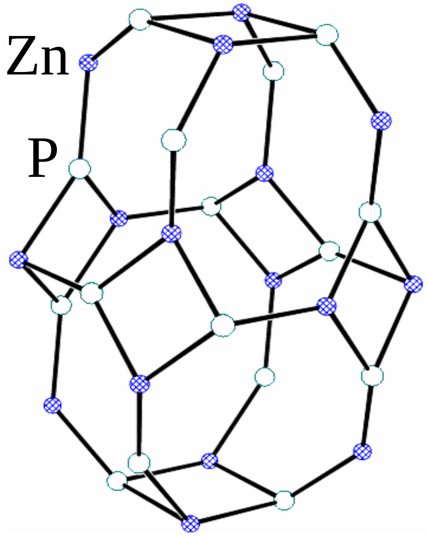
4-membered ring



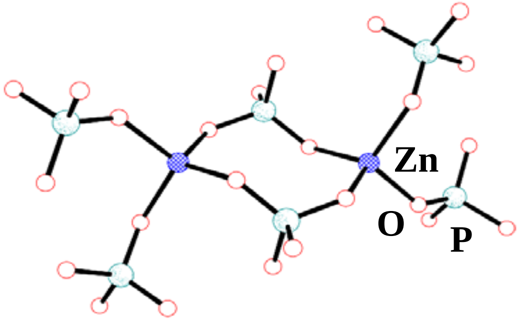
Interrupted Sodalite



Sodalite

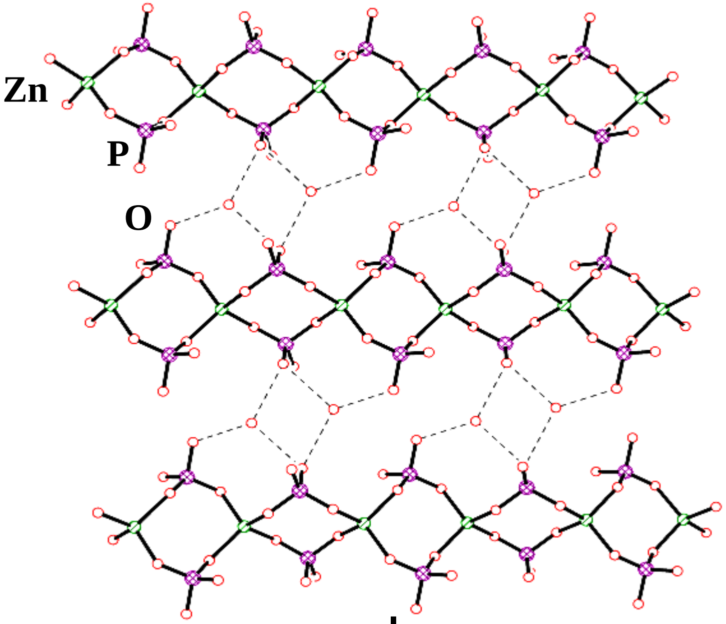


Expanded Sodalite



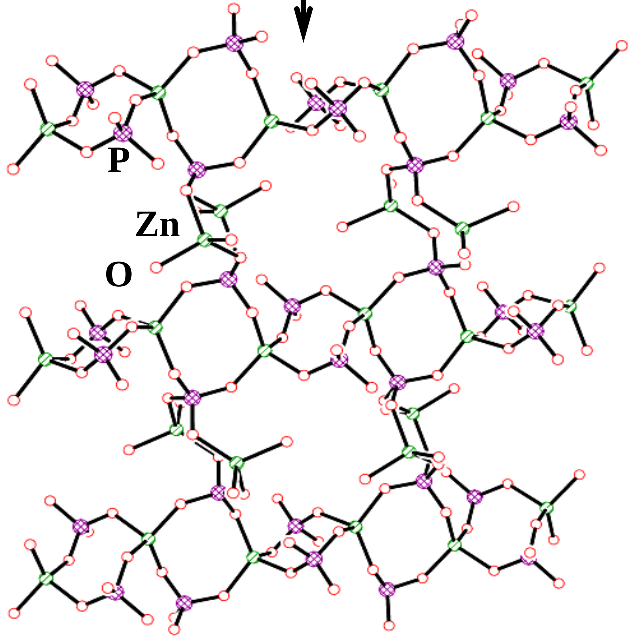
Monomer

$\xrightarrow[30°C]{PIP}$



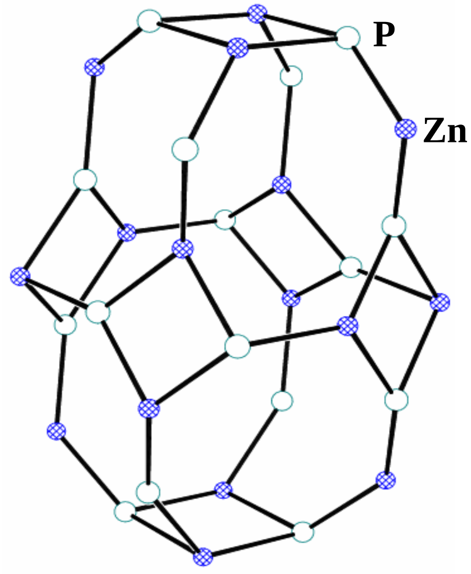
Corner sharing 4-membered ring chains

PIP ↓ 50°C



Single layer of the 3-dimensional structure

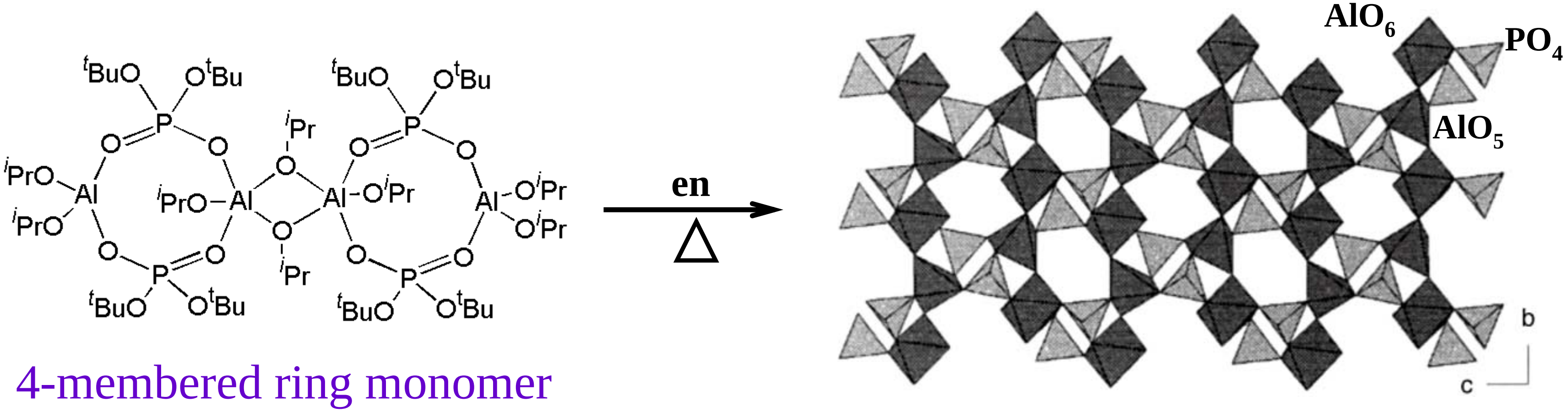
≡



Sodalite-related structure

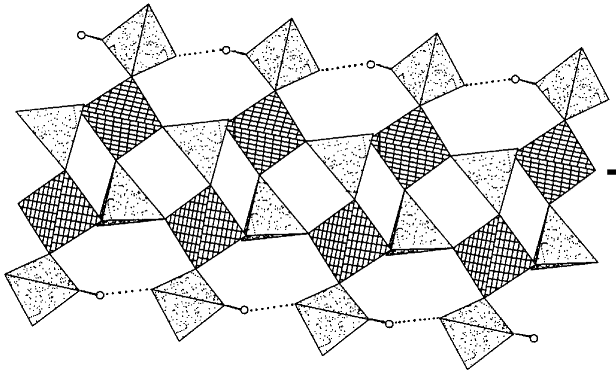
Dan & Rao *Chem. Commun.*, 2003

Transformation studies on Aluminophosphates



4-membered ring monomer

|||

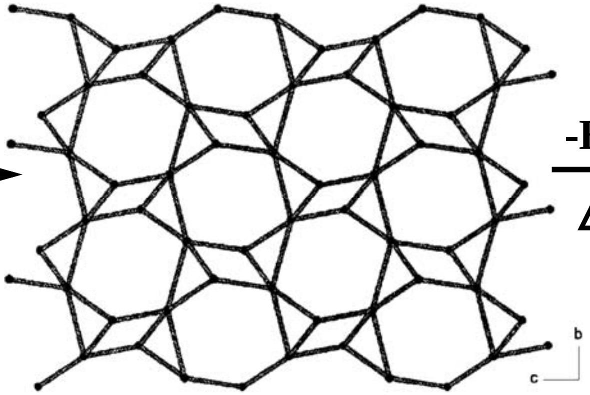


4-membered ring ladder, $[C_2N_2H_{10}][Al(PO_4)(HPO_4)]$

Ruren Xu et. al.

en

Δ

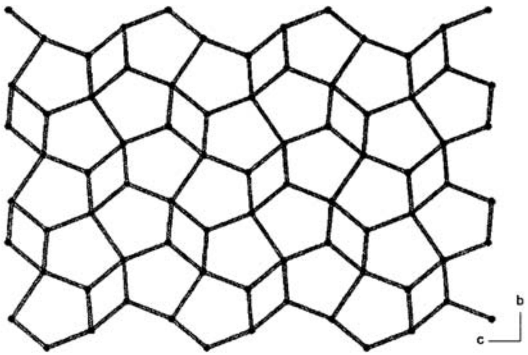


2-D layered structure, $[C_2N_2H_{10}][Al_2(OH)_2(PO_4)_2].H_2O$, containing SBU-4 formed

Fjellvag et. al.

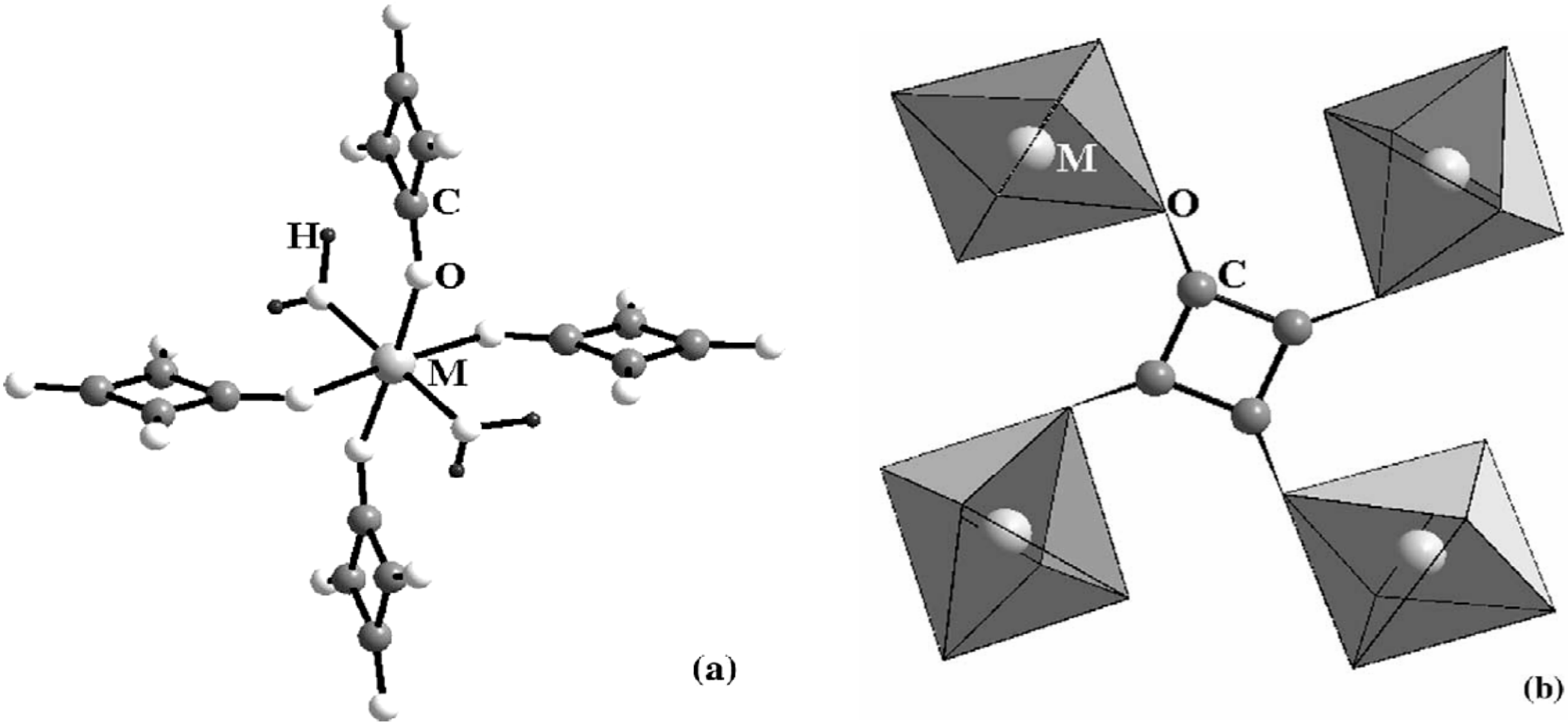
$-H_2O$

Δ

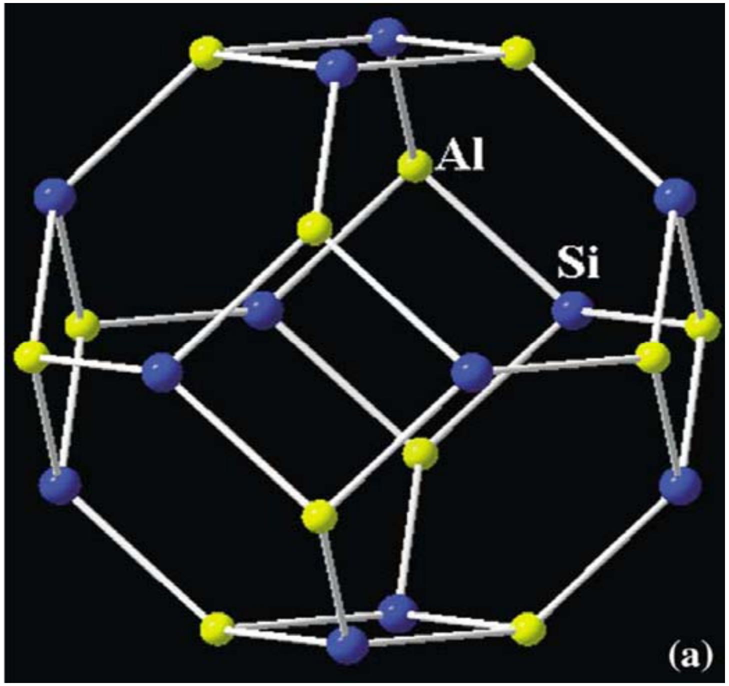


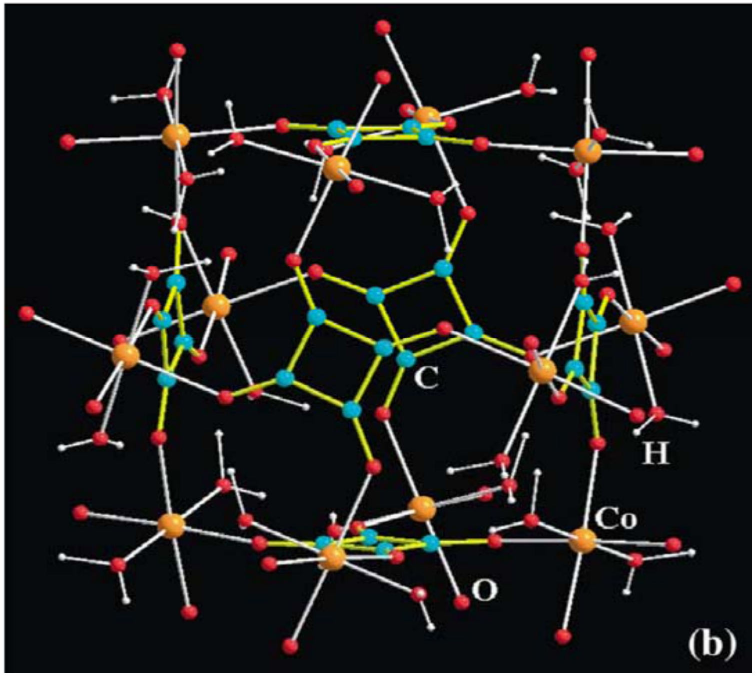
2D layer of the composition $[C_2N_2H_{10}][Al_2O(PO_4)_2]$

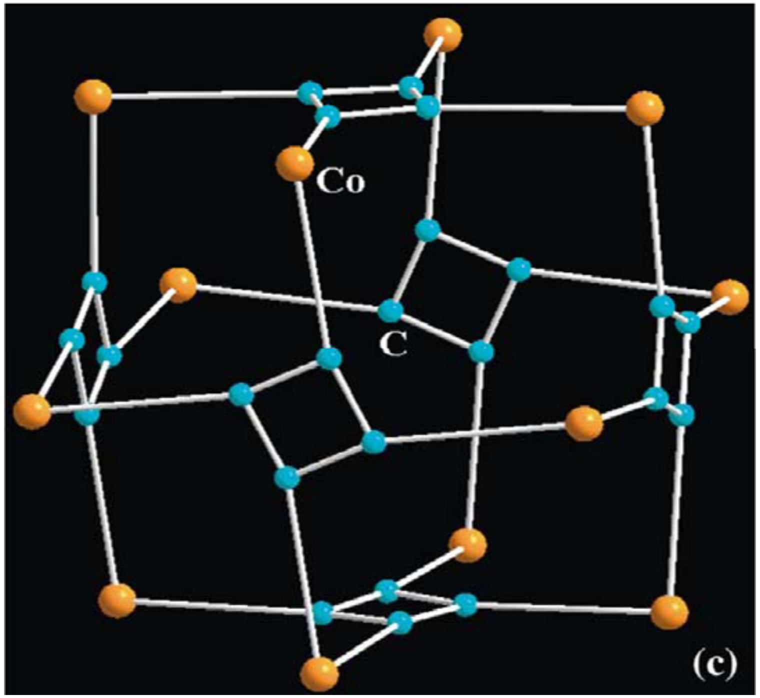
Murugavel, Roesky, Dan, C. N. R. Rao, *Acc. Chem. Res.*, 2004, 37, 763

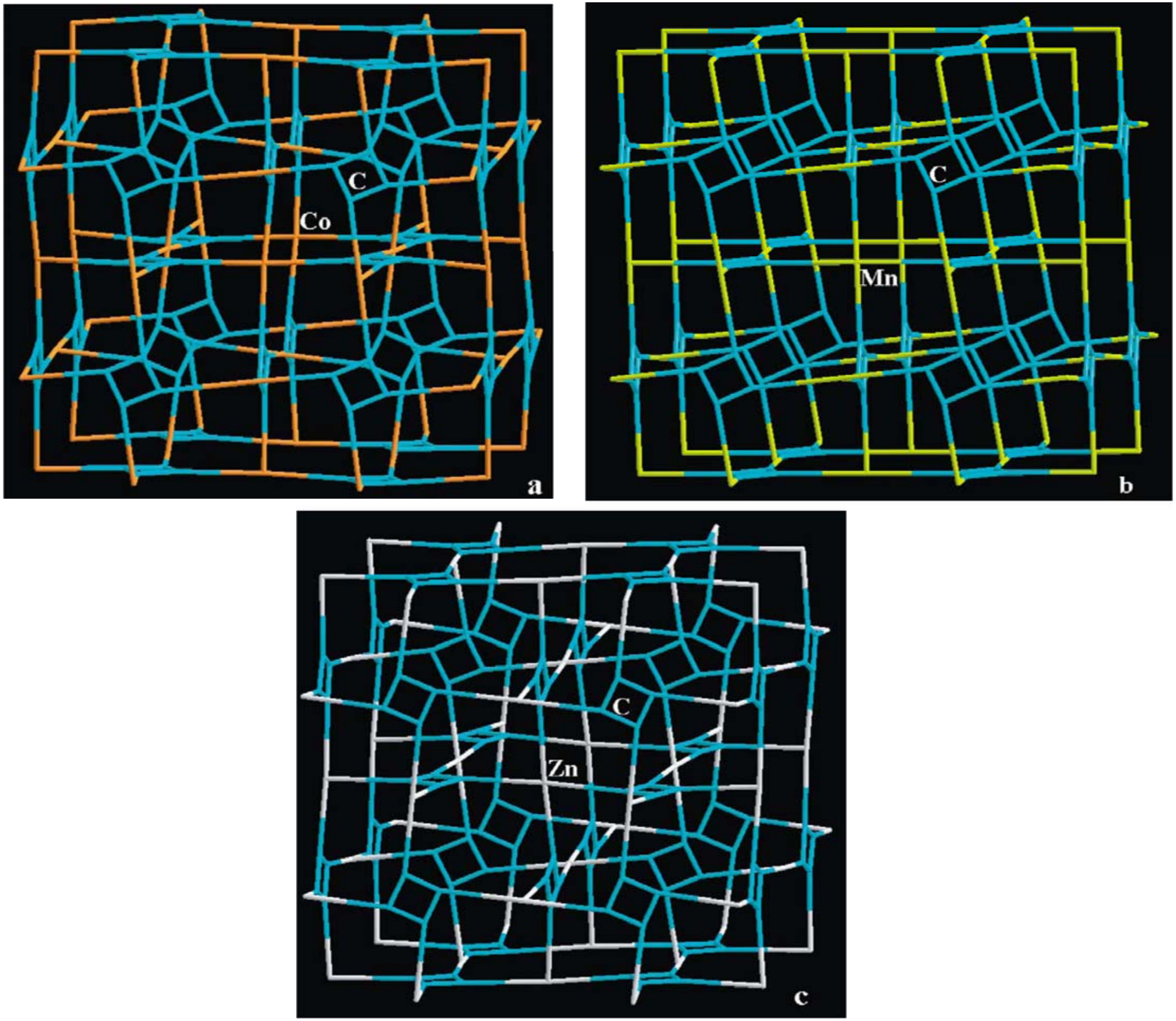


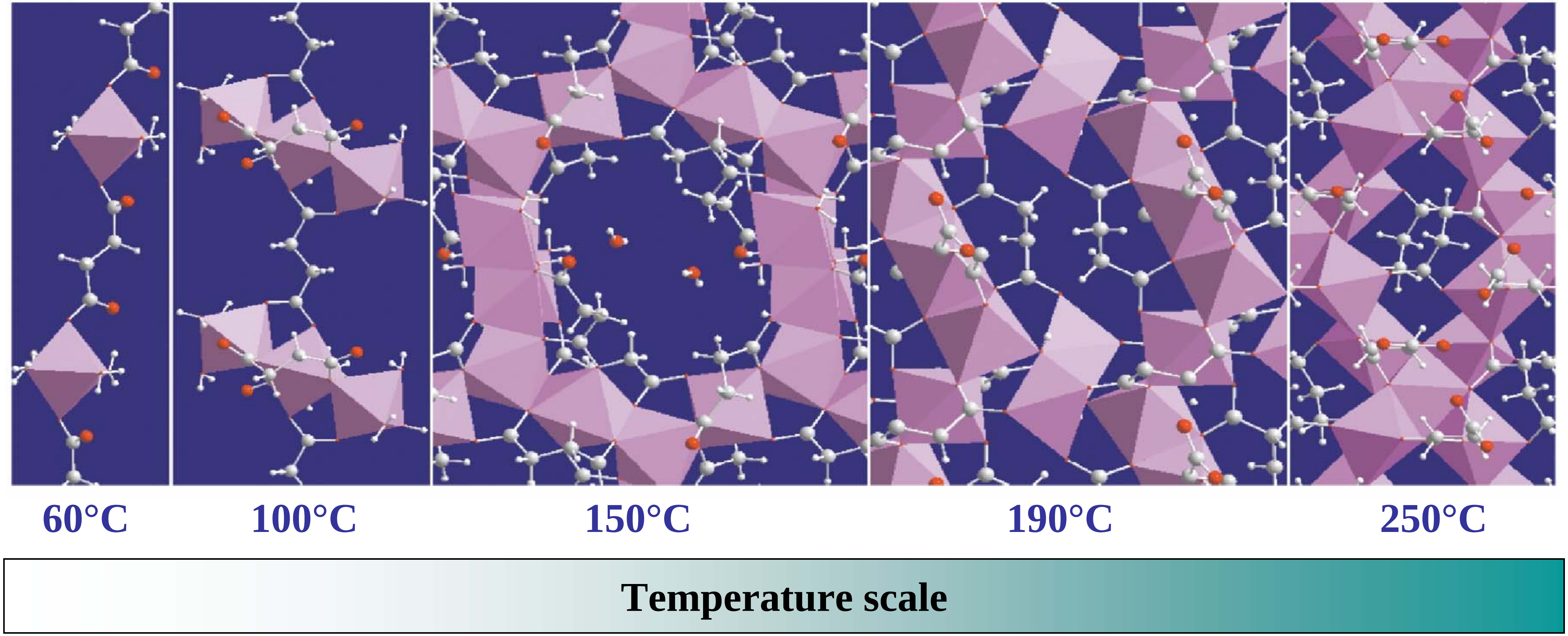
Neeraj, Cheetham & Rao (2002)


Al
Si
(a)


C
H
Co
O
(b)


Co
C
(c)

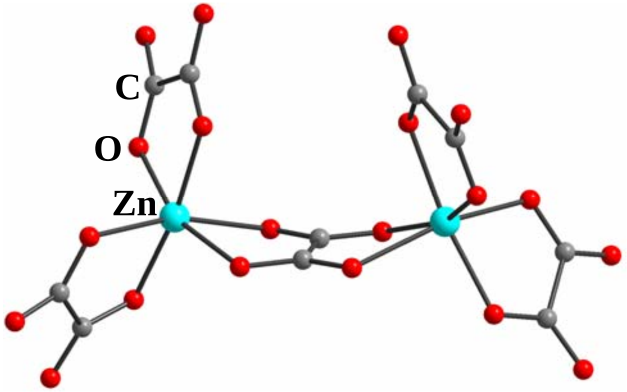

C
Co
a
C
Mn
b
C
Zn
c



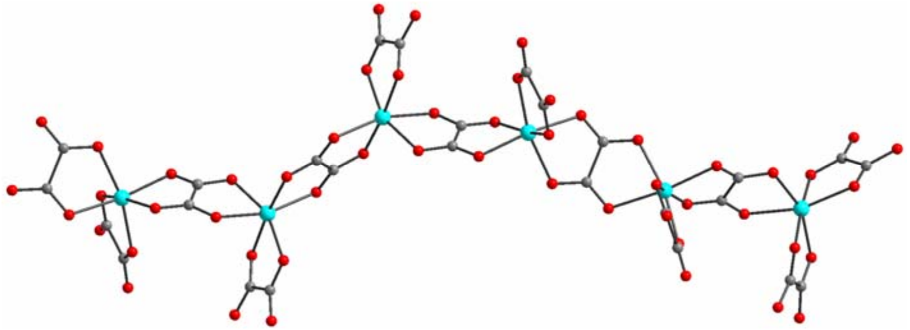
Synthesis Temp.	Phase	Dim.	M-O-M dim.	Total H_2O content	No. of H_2O coordinated to Co
60	$Co(H_2O)_4(C_4H_4O_4)_2$	1	0	4	4
100	$Co(H_2O)_2(C_4H_4O_4)_2$	1	0	2	2
150	$Co_4(H_2O)_2(OH)_2(C_4H_4O_4)_3{\cdot}2H_2O$	2	2	1	1/2
190	$Co_6(OH)_2(C_4H_4O_4)_5{\cdot}_2H_2O$	3	2	1/3	0
250	$Co_5(OH)_2(C_4H_4O_4)_4$	3	2	0	0

Cheetham & Foster

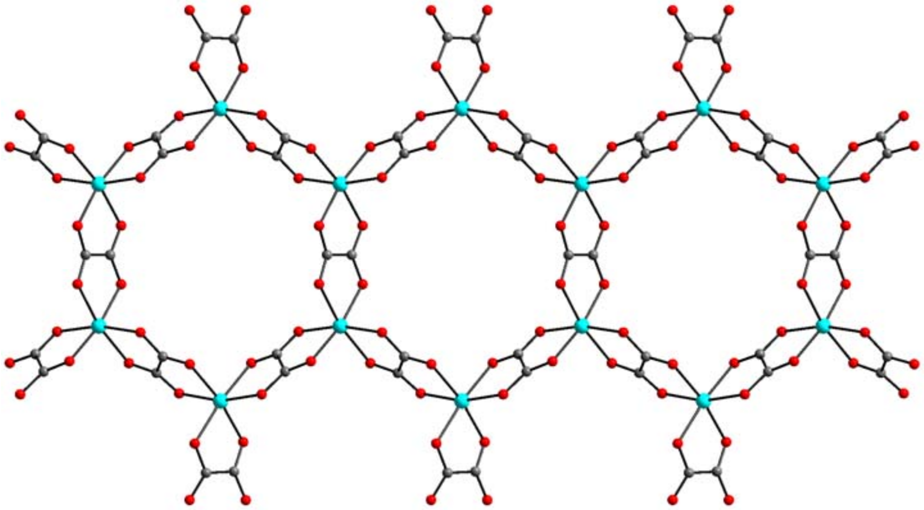
Zinc Oxalates



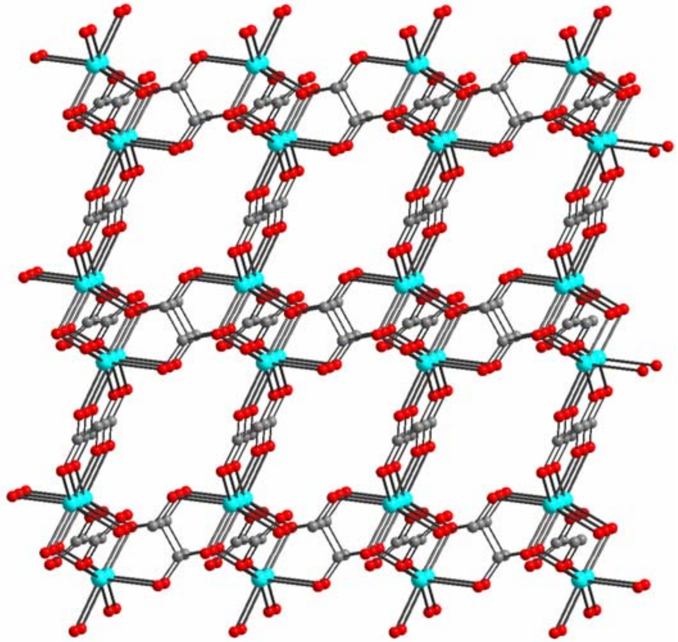
Dimer, $[Zn_2(C_2O_4)_5][C_4N_2H_{12}]_3.8H_2O$, I



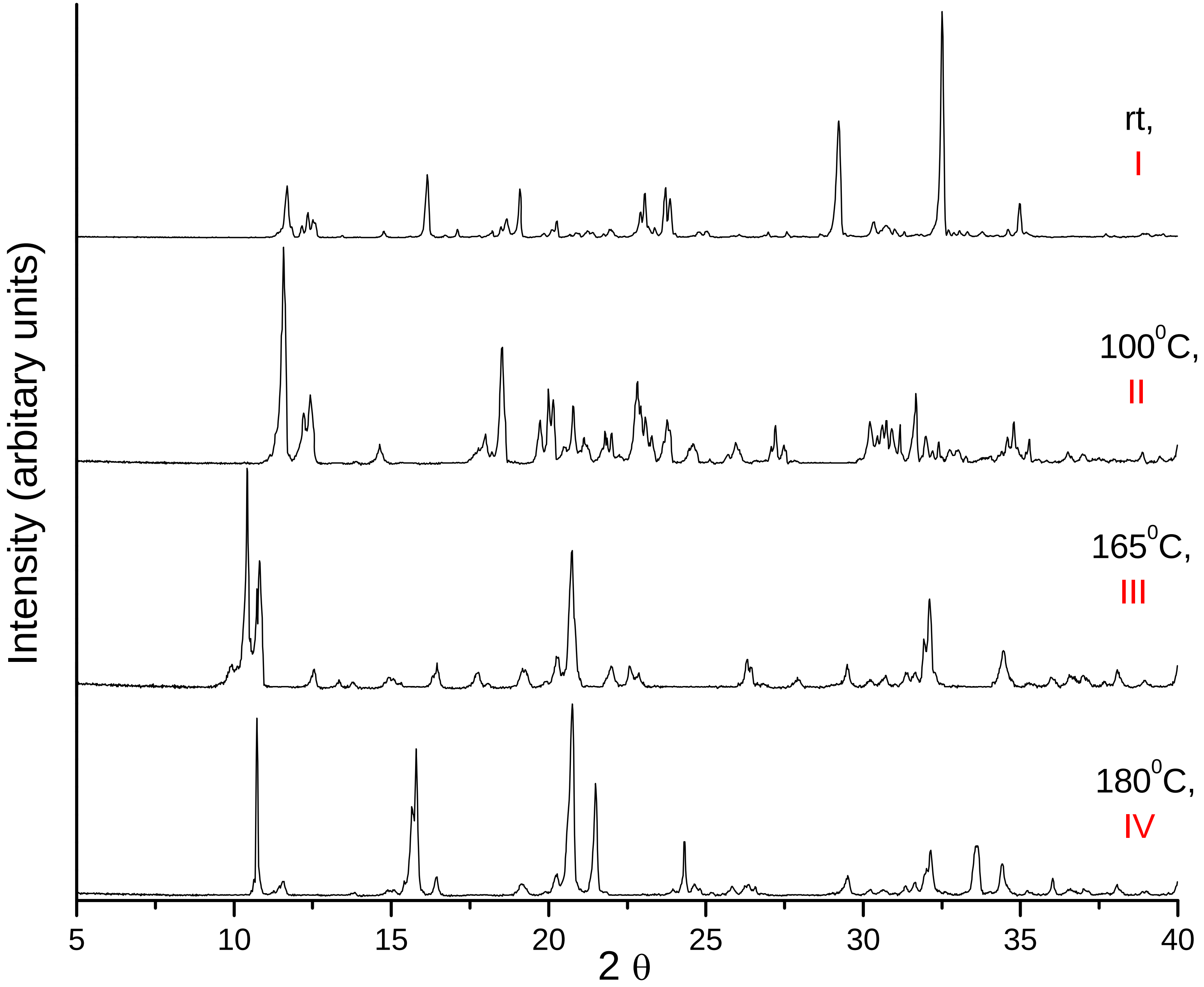
Chain, $[Zn_2(C_2O_4)_4][C_4N_2H_{12}]_2.3H_2O$, II

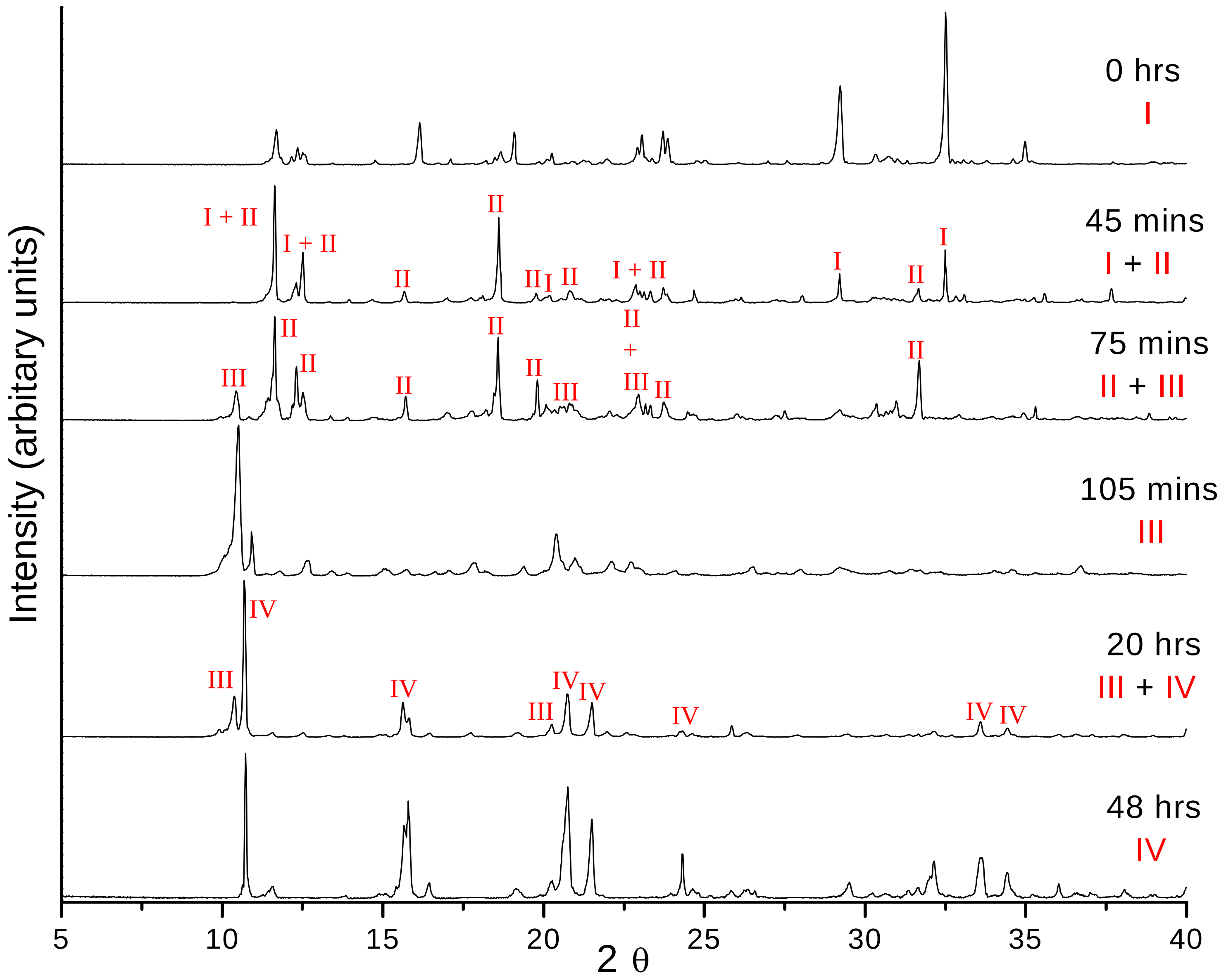


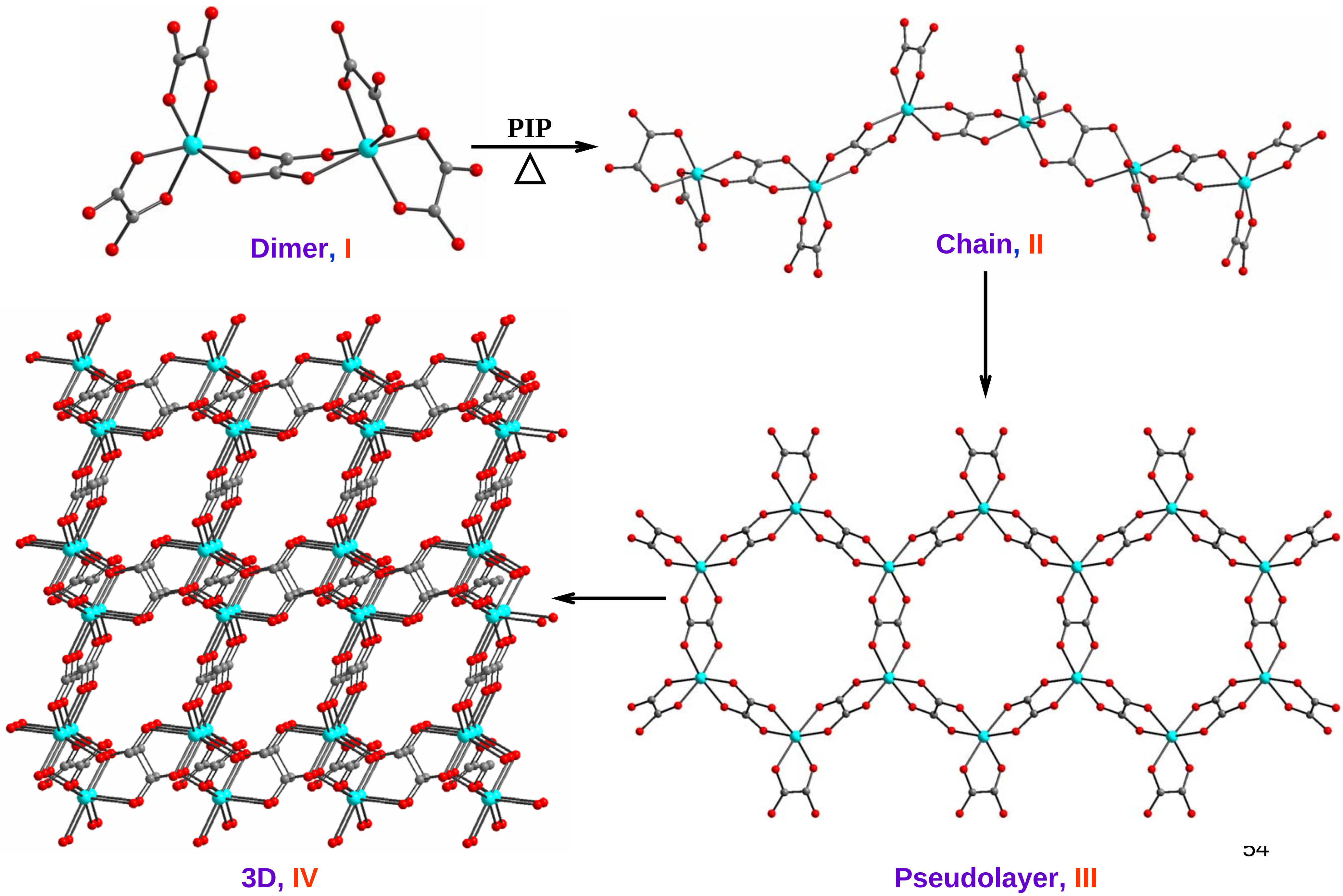
Pseudolayer, $[Zn_4(C_2O_4)_7][C_4N_2H_{12}]_3.4H_2O$, III



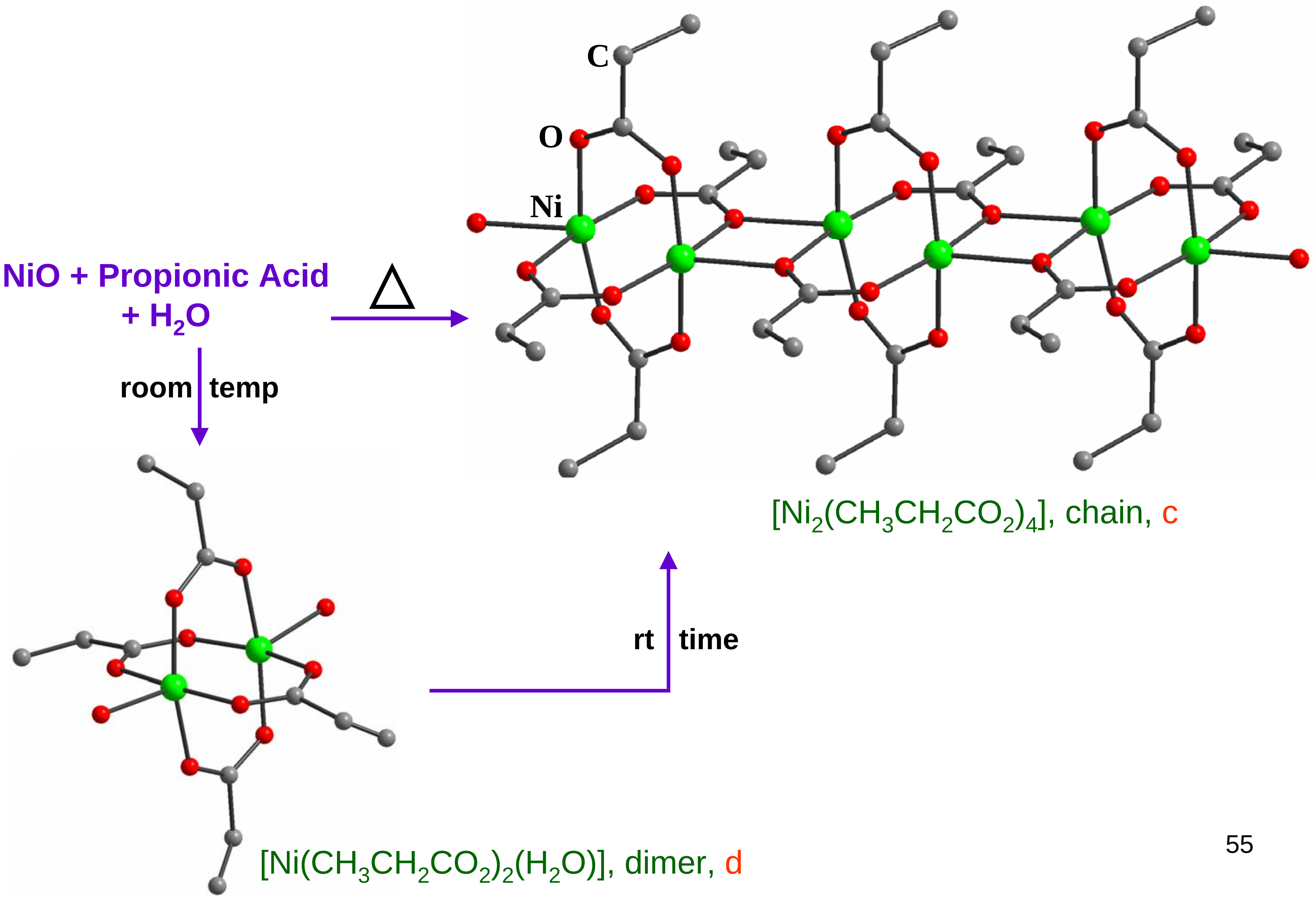
3D, $[Zn_2(C_2O_4)_3][C_4N_2H_{12}]$, IV


rt,
I
100^{0}C,
II
165^{0}C,
III
180^{0}C,
IV
Intensity (arbitary units)
5
10
15
20
25
30
35
40
2 θ


Intensity (arbitary units)
0 hrs
I
45 mins
I + II
I + II
I + II
II
II
II
I
II
I + II
I
II
I
75 mins
II + III
III
II
II
II
II
II
III
II
+
III
II
II
105 mins
III
20 hrs
III + IV
III
IV
IV
III
IV
IV
IV
IV
IV
48 hrs
IV
5
10
15
20
25
30
35
40
2 θ


Dimer, I
PIP
Δ
Chain, II
Pseudolayer, III
3D, IV

Nickel Propionate



NiO + Propionic Acid + H_2O

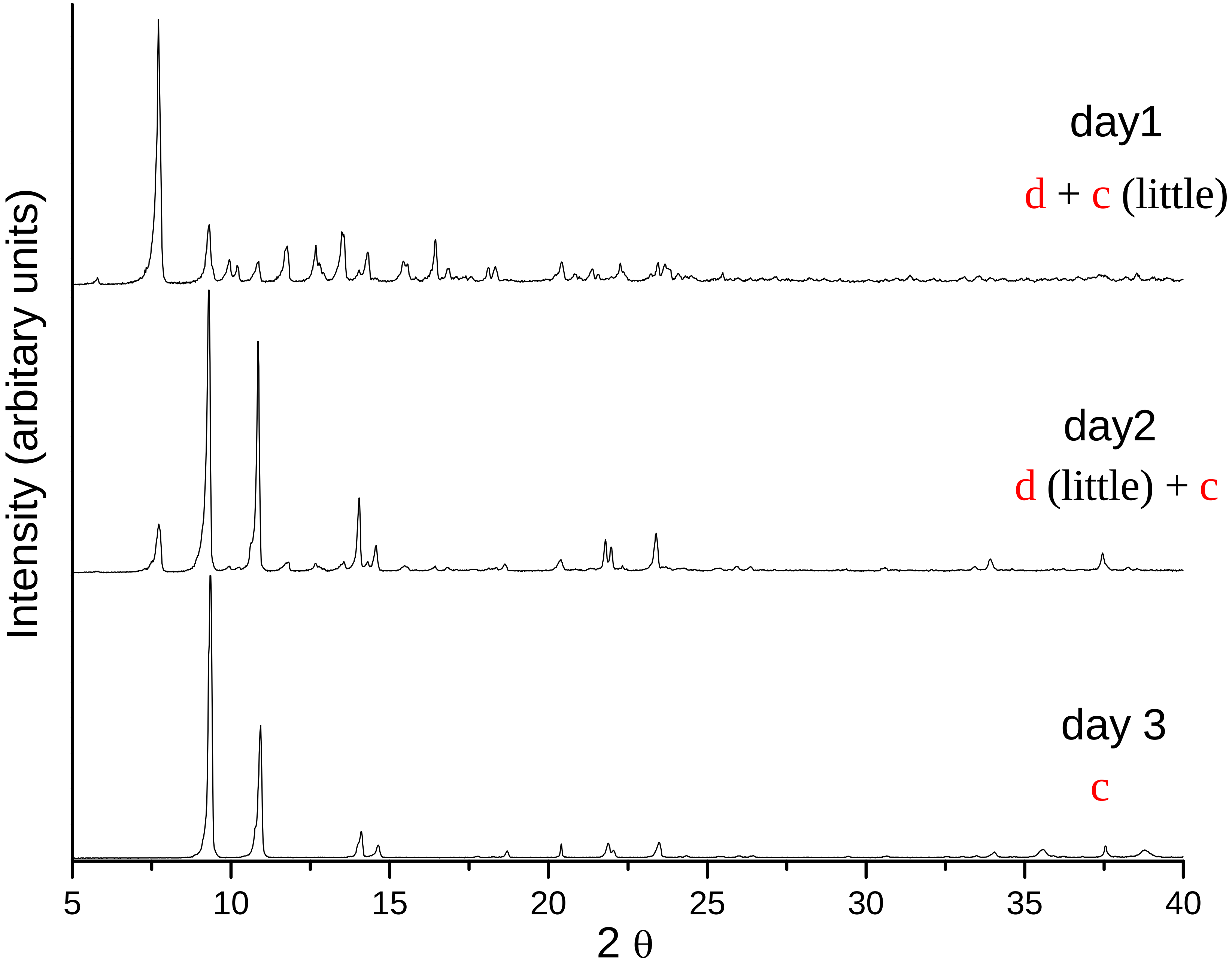
Δ

room temp

rt time

$[Ni_2(CH_3CH_2CO_2)_4]$, chain, c

$[Ni(CH_3CH_2CO_2)_2(H_2O)]$, dimer, d


Intensity (arbitary units)
day1
d + c (little)
day2
d (little) + c
day 3
c
5
10
15
20
25
30
35
40
2 θ

Thank You