Topological Characterization of Coordination Networks & Metal-Organic Frameworks: nets and entanglements in periodic structures

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The Geometrical Basis of Crystal Chemistry. Part 1

BY A. F. WELLS

Imperial Chemical Industries Limited (Dyestuffs Division), Hexagon House, Manchester 9, England

(Received 1 January 1954 and in revised form 1 April 1954)

An investigation is made of the periodic three-dimensional systems of points in which each point is connected to three others. These nets form the basis of the structures of a large number of crystals in which there are directed bonds or hydrogen bonds.

Further Studies of Three-dimensional Nets

A.F. Wells ACA Monograph No. 8
From the framework of alumino-silicates we get a net by removing all 2-coordinated oxygen atoms -T-O-T-.
Mineralomimetic chemistry as a modern aspect of co-ordination chemistry

Toschitake Iwamoto,*+ Shin-ichi Nishikiori, Takafumi Kitazawa and Hidetaka Yuge

Mineralomimetic chemistry:

mineralomimetic structures are represented by nets observed in minerals
Design and Construction of a New Class of Scaffolding-like Materials Comprising Infinite Polymeric Frameworks of 3D-Linked Molecular Rods. A Reappraisal of the Zn(CN)₂ and Cd(CN)₂ Structures and the Synthesis and Structure of the Diamond-Related Frameworks [N(CH₃)₄][Cu¹Zn¹¹(CN)₄] and Cu¹[4,4',4'',4'''-tetracyanotetraphenylmethane]BF₄·xC₆H₅NO₂

B. F. Hoskins and R. Robson* 953 citations

Contribution from the Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia. Received July 12, 1989
early ’90

Crystal Engineering
Crystal Design

Infinite Polymeric Frameworks

Coordination (Polymers) Networks

Organic/Inorganic Hybrid Materials

Metal Organic Frameworks (MOFs)

Supramolecular Architectures
Different frameworks could be obtained on changing the coordination/H-bond geometry of the nodes...
Metal ions: Ag, Cu, Ni, Co, Zn, Cd…

coordination number and geometry

Ligands

donors: N, O, P, S
bi/polidentate
neutral/anionic
Length
rigidity/flexibility
Kinoshita, Y., Matsubara, I., Higuchi, T. and Saito, Y. *Bull. Chem. Soc. Jpn* 1959, 32, 1221

Coordination Network

\[
[Cu(NC\text{}_{2})\text{CN}]_{2}\text{NO}_3
\]

multiply intergrown *aka* interpenetrated (6-fold)

underlying net: diamondoid (dia)

Kinoshita, Y., Matsubara, I., Higuchi, T. and Saito, Y. *Bull. Chem. Soc. Jpn* 1959, 32, 1221
Coordination Network with polytopic links

Design and synthesis of an exceptionally stable and highly porous metal-organic framework

Hailian Li*, Mohamed Eddaoudi†, M. O’Keeffe* & O. M. Yaghi†
Metal-Organic Frameworks (MOFs)

1) Cationic metal-containing clusters (secondary building units SBU)

2) Joined by organic linkers

3) Neutral frameworks

4) Robust and highly porous
1) Cationic metal-containing clusters (secondary building units SBU)

The cluster in basic zinc acetate

In the acetate each carboxylate C atom (black) is joined to a methyl group -> discrete molecule

In MOF-5 the basic zinc acetate clusters (SBU) are joined by ditopic linkers (terephthalate) to make an infinite crystal (neutral framework) that is robust and highly porous.

Architectural stability of MOF-5
Coordination Networks

Metal Organic Frameworks MOFs

Covalent Organic Frameworks COFs

Supramolecular Architectures

*Interactions*

Covalent, Ionic, Coordination

H-bond, van der Waals

CH···O, CH···π, π···π

...end of the nineties

1998 IF 4.00

2000 IF 4.39
MOF-like structures reported in the CSD (Cambridge Structural Database)

Doubling time 3.6 yrs compared with 9.3 yrs for all CSD!

# of structures in CSD Nov 2010: 531715
Reticular Chemistry

2375 citations

Scale Chemistry

974 citations
Underlying nets

Standard representation:
Keep only atoms with coordination > 2

Cluster representation:
Simplification of polydentate groups or SBU with centres of the same coordination
simplification and rationalization.....

**Topology** is the theory of shapes which are allowed to stretch, compress, flex and bend, but without tearing or gluing.

2D hexagonal honeycomb layer “hcb”

brick wall

parquet
SbCl₃(ρ-diacetylbenzene)
Cationic clusters and SBUs (red)

SBU = Secondary Building Unit. Blue polyhedra are Metal-O
Organic polytopic linkers (top) and **SBUs** (bottom, green)
Two simplest type of MOF topology

(a) MOF-5 underlying net
   6-c pcu

(b) underlying net
   3,4-c pto

“Cluster representation”
program package for multipurpose crystallochemical analysis

TOPOS

Version 4.0
PRACTICAL MANUAL 1.0.4
V.A. Blatov & D.M. Proserpio
revision 23/4/2011

Simplification of any periodic structure and classification of the underlying net
... and much more

http://www.topos.ssu.samara.ru/

Commission on Crystallographic Computing
International Union of Crystallography
Newsletter No. 7, November 2006
"Understanding Crystal Structures"
Dia, PCU, PTO

Three letter symbols are RCSR symbols

Reticular Chemistry Structure Resource
rcsr.anu.edu.au

M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi
Coordination Networks & MOFs

...but which nets are more important and/or frequent and/or likely to occur?
Q. What are the ways of linking simple shapes (squares, tetrahedra etc.) into frameworks?
A. Infinitely many

Q. Of these what are the most likely targets for synthesis?
A. Those with one kind of link (edge transitive)

Q. How many of these?
A small number: 54 edge transitive nets
these are the prime targets of reticular chemistry

O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi
5 special uninodal have regular coordination figure

15 other nets with one kind of vertex and one kind of edge
34 other nets with two kinds of vertex and one kind of edge

equilateral triangle
square
regular tetrahedron
regular octahedron
equilateral triangle
regular tetrahedron
regular octahedron

cube

srs
nbo
"srssrs"
"nbonbo"
"bcsbcu"
"fcsfcu"
"pcupcu"
Most frequent underlying nets

2004
Interpenetrating metal–organic and inorganic 3D networks: a computer-aided systematic investigation. Part I. Analysis of the Cambridge structural database†‡

V. A. Blatov,*,a L. Carlucci,*,b G. Ciani*b and D. M. Proserpio*a,b

Reticular Chemistry: Occurrence and Taxonomy of Nets and Grammar for the Design of Frameworks
NATHAN W. OCKWIG,† OLAF DELGADO-FRIEDRICH,*‡ MICHAEL O’KEEFFE,*‡ AND OMAR M. YAGHI,*‡

CrystEngComm, 2011, 13, 3947–3958
Underlying nets in three-periodic coordination polymers: topology, taxonomy and prediction from a computer-aided analysis of the Cambridge Structural Database†‡

E. V. Alexandrov,*, V. A. Blatov,*,a A. V. Kochetkov* and D. M. Proserpio*a,b

default nets

1° pcu
2° dia
3° bcu
4° cds
5° srs
...
16° nbo

301 CNs
774 MOFs
6620 CNs
11651
We feel that we discovered, rather than invented, the five regular nets. The present discovery that Nature uses these structures overwhelmingly in crystal topologies does not surprise us; rather it is the exceptions that are the occasions for thought.
But it’s all so ... simple?

*nets* and *entanglements*

in periodic structures

Entangled: interlaced; complicated;
Entanglement: intricate and confused involution

*interpenetration and* *polycatenation*
Interpenetrating Diamondoid Frameworks of Silver(i) Cations Linked by $N,N'$-Bidentate Molecular Rods

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Three novel coordination polymers, [Ag(N=N)$_2$]X (N=N = 4,4'-bipyridyl, X = CF$_3$SO$_2$; 1; N=N = 4-cyanopyridine, X = BF$_4$; in two polymorphs, 2 and 3), are prepared and investigated by single crystal X-ray analysis; 1 and 2 contain three-dimensional cationic frameworks, both consisting of four equivalent interpenetrating diamondoid lattices, while 3 is formed by two-dimensional layers of distorted squares.

Received, 26th September 1994;

Fig. 1 A view of a single adamantoidal cage of 1. Note, one of the two independent 4,4'-bipy ligands is not planar and gives one bent interaction with the Ag$^+$ ions.

Fig. 2 A schematic view of the four equivalent interpenetrating diamondoid frames in 2. Only one set of stacked ligands (interplanar distance of 4.0 Å) is shown for clarity.
Interpenetrating structures, are characterized by the presence of infinite structurally regular motifs that must contain rings through which independent components are inextricably entangled and that can be disentangled only by breaking internal connections.
Polycatenation, polythreading and polyknotting in coordination network chemistry

Lucia Carlucci, Gianfranco Ciani, Davide M. Proserpio

Borromean links and other non-conventional links in ‘polycatenated’ coordination polymers: re-examination of some puzzling networks

Lucia Carlucci, Gianfranco Ciani, Davide M. Proserpio


V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio

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First published as an Advance Article on the web 17th September 2004
interpenetration of dia nets
Cuprite $\text{Cu}_2\text{O}$  Niggli 1922
Crystallographic observation: typically interpenetrated nets are generated from one independent atom.

What are the symmetry relations among the interpenetrated sub-nets?

Can we find a systematic way to classify all the possible 3D interpenetration phenomena?

YES using TOPOS....
**Class I (a,b)**

*Nets related* only by translation

**Class II (a,b)**

*Nets related* only by non-translational *symmetry elements*

**Class III (a,b,c,d)**

*Nets related by* translational and non-translational *symmetry elements*
Class I

Nets related by translation only
[Ag(1,4-butanedinitrile)$_2$](X) X = BF$_4^-$, ClO$_4^-$, PF$_6^-$, AsF$_6^-$, SbF$_6^-$

related by Translations
Class Ia

Diamondoid-5f
Class II

Nets related only by non-translational symmetry elements
Design and structural analysis of interpenetrated 3-D co-ordination networks formed by self-assembly using tetrapyridinocyclophane and silver cations

Cédric Klein, Ernest Graf, Mir Wais Hosseini* and André De Cian

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First published as an Advance Article on the web 18th January 2001
dia 4-fold related by screw axis 4₁
Class IIb
Class III (a,b,c,d)
Nets related by
translational AND non-translational
symmetry elements
[ZnL₂](ClO₄)₂
(1996/2002)

dia 6-fold related by translation AND non-translational sym. op.
Class IIIa

TIV = [1/2, 1/2, 1/2]

Zt = 3

6(3*2)

\(\bar{1}\)
Net occurrences:
Leader again the default nets!
dia, pcu, srs

965 interpen nets

World Records
2008 12-fold dia CN
2009 18-fold dia H-bond
2011 54-fold srs CN

degree of interpenetration

965 up to 2009
... and now a natural question:

Are these classes topologically related?

i.e. can we deform one member of a class into a member of another class?

For instance we know 38 examples of diamondoid coordination network that are 4-fold interpenetrated....

How many are topologically distinct?
38 examples of dia 4-fold
observed in 5 classes

We get only 2 distinct topological types

(work in progress)
Can we entangle 1D or 2D nets in a different way (topological)?

*Interpenetration* vs. *Polycatenation*
$2D + 2D \rightarrow 2D$

interpenetrated 3-fold

3D

polycatenated parallel

3D

polycatenated inclined
Inexorable Entanglement
via Hopf links

1D + 1D $\Rightarrow$ 2D/3D
2D parallel $\Rightarrow$ 2D
2D inclined $\Rightarrow$ 3D
3D $\Rightarrow$ 3D

increase of dimensionality

Interpenetration

Polycatenation

dimensionality unchanged
dimensionality unchanged: **INTERPENETRATION**

the whole has the **SAME** dimensionality of the components

the number of entangled components is finite (n-fold)

each component is interlaced with ALL the others

increase of dimensionality: **POLYCATENATION**

the whole has **HIGHER** dimensionality of at least one component

the number of entangled components is infinite

at least one component is not interlaced with all the others

the difference in not only semantic... but is topologic
TOPOS

The zeolite conundrum: why there are so many hypothetical zeolites and so few are observed?
N. A. Anurova, V.A. Blatov, G.D. Ilyushin, D.M. Proserpio

Nanocluster description of intermetallics
V.A. Blatov, G.D. Ilyushin, D. M. Proserpio
Inorg. Chem. 2010, 49, 1811–1818
V.A. Blatov, G.D. Ilyushin, D. M. Proserpio
1.3 Networks, Topologies, and Entanglements
Lucia Carlucci, Gianfranco Ciani, and Davide M. Proserpio

1 Periodic-Graph Approaches in Crystal Structure Prediction
Vladislav A. Blatov and Davide M. Proserpio

2007

2011