

Terminology of metal–organic frameworks and coordination polymers (IUPAC Recommendations 2013)*

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Abstract: A set of terms, definitions, and recommendations is provided for use in the classification of coordination polymers, networks, and metal–organic frameworks (MOFs). A hierarchical terminology is recommended in which the most general term is coordination polymer. Coordination networks are a subset of coordination polymers and MOFs a further subset of coordination networks. One of the criteria an MOF needs to fulfill is that it contains potential voids, but no physical measurements of porosity or other properties are demanded per se. The use of topology and topology descriptors to enhance the description of crystal structures of MOFs and 3D-coordination polymers is furthermore strongly recommended.

Keywords: coordination chemistry; coordination networks; coordination polymers; inorganic chemistry; IUPAC Inorganic Chemistry Division; materials chemistry; metal complexes; metal–organic frameworks (MOFs); nanostructured materials; polymers.

INTRODUCTION

Coordination polymers [1] and metal–organic frameworks [2,3], colloquially known as MOFs, constitute an interdisciplinary field with its origins in inorganic and coordination chemistry that has expanded rapidly the last two decades, and is now also attracting the interest of the chemical industry [4,5].

The diversity in both the focus and the scientific base of those involved has led to a variety of terminological usages for this class of compounds, and of several subgroups within; a disquieting number

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of abbreviations are also in use. Moreover, the nomenclature used to name networks is not consistent among research groups, causing additional confusion and unnecessary misunderstandings.

The IUPAC task group Coordination Polymers and Metal Organic Frameworks: Terminology and Nomenclature Guidelines has since 2009 documented, analyzed, and evaluated existing practices in a continuous dialogue with researchers in the field. This is the final report of this group.

In passing we note, as we perceive it, a slight problem with paragraph IR-9.1.2.2 of the “Red Book”, the *2005 IUPAC Recommendations for the Nomenclature of Inorganic Chemistry*. This paragraph states that for nomenclature purposes:

“A coordination compound is any compound that contains a coordination entity. A coordination entity is an ion or neutral molecule that is composed of a central atom, usually that of a metal, to which is attached a surrounding array of atoms or groups of atoms, each of which is called ligands.” [6]

As it is also useful to consider some boron compounds, as well as some main group compounds as coordination compounds, the wording “usually that of a metal” appears in this paragraph. However, it may be interpreted in a more all-encompassing way than was originally intended, for example, methane is not a coordination compound, but could nevertheless be considered to fit this definition. It is not immediately clear that a better definition can be formulated, however, and the question lies outside the task group’s jurisdiction.

A note on the figures illustrating various examples: If possible, a line drawing depicting the smallest repeating unit (the “monomer”) has been included with the lines drawn through the parentheses indicating the propagation of the polymer. The X-ray structure drawings depict various truncated parts of the compounds, usually containing several monomers.

RECOMMENDATIONS

Coordination polymer

Definition

A coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.

Comment

Coordination polymers do not need to be crystalline; therefore, the more appropriate terms (for crystalline states) 1-periodic, 2-periodic, and 3-periodic cannot be used throughout. These compounds may in some cases, such as those being composed of mainly carboxylates, even be regarded as salts. The prefix 1D-, 2D-, or 3D- is acceptable for the indicating the degree of extension of the coordination polymer.

Furthermore, when using this term it should be kept in mind that the IUPAC definition of “polymer” is more inclusive than the colloquial use it has among chemists and engineers. The current recommendations are as follows [7]:

Polymer: A substance composed of macromolecules

Polymer molecule (macromolecule): A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

For an extensive discussion of definitions the reader is referred to a more detailed argument in the task group’s *CrystEngComm* article [8]. Briefly, the general idea is that a single chain of polyethylene is a “polymer molecule”, and that many individual polyethylene chains make up a polymer. When a compound is cross-linked in 3D the distinction disappears. For coordination polymers it is reasonable to assume, and sometimes proven, that in solution, or indeed in a precrystalline state, if we do solid-state synthesis, there are polynuclear entities that without doubt can be called (polymer) macromolecules. These then crystallize or polymerize into the coordination polymer.

Example

A classical type of single-chain coordination polymer is the (4,4'-bipyridine-*N,N*)-bridged cobalt(II) compound depicted in Fig. 1 [9]. Names of this and other example compounds are left out of the main text, as new IUPAC recommendations are being prepared for these materials.

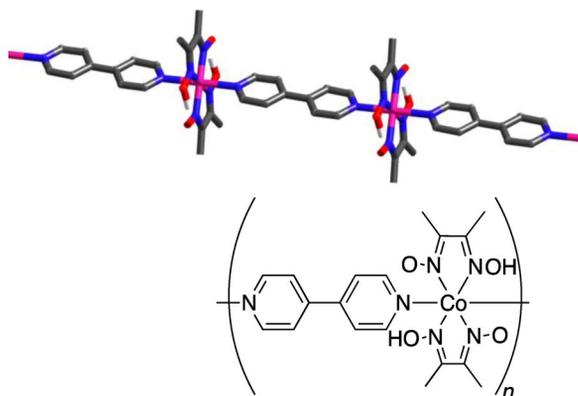


Fig. 1 An example of a 1D-coordination polymer [9]. Hydrogen atoms on carbon have been left out for clarity. Names of this and other example compounds are left out of the text, as new IUPAC recommendations are being prepared for such compounds. Mauve: Co; blue: N; red: O; grey: C; white: H.

Coordination network*Definition*

A coordination compound extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions.

Comment

The preferred and most widely understood term will likely be: “coordination polymer”. However, IUPAC endorses also the use of the term “coordination network”, even though it should be clear that these two terms are not synonymous and that coordination network is in fact a subset of coordination polymer.

Examples

As nets can also be formed by cross-links between single chains as shown in Fig. 2, loops as shown in Fig. 3, or spiro-links, an example of which is displayed in Fig. 4, these type of compounds also belong to the coordination networks, while still extending only in 1 dimension and therefore also being 1D-coordination polymers. In Fig. 5 we show a classical 3D-coordination polymer.

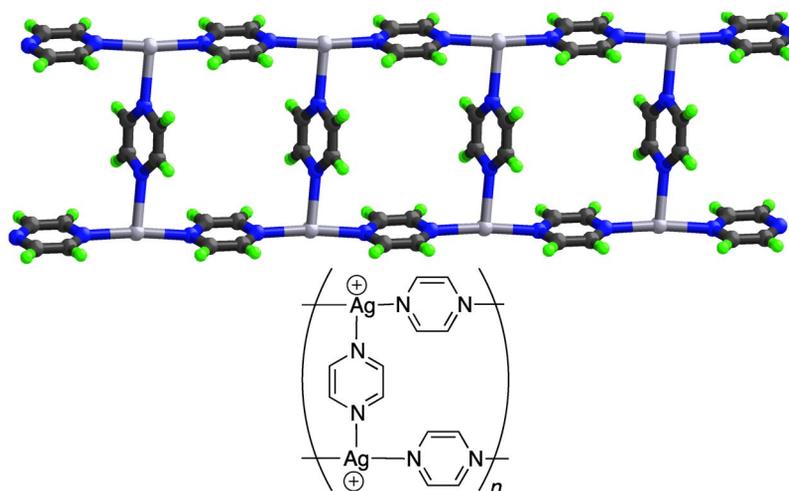


Fig. 2 Example of cross-links forming a coordination network, the weakly coordinating trifluoromethane-sulfonate anions are not shown [10]. Light grey: Ag; blue: N; grey: C; green: H.

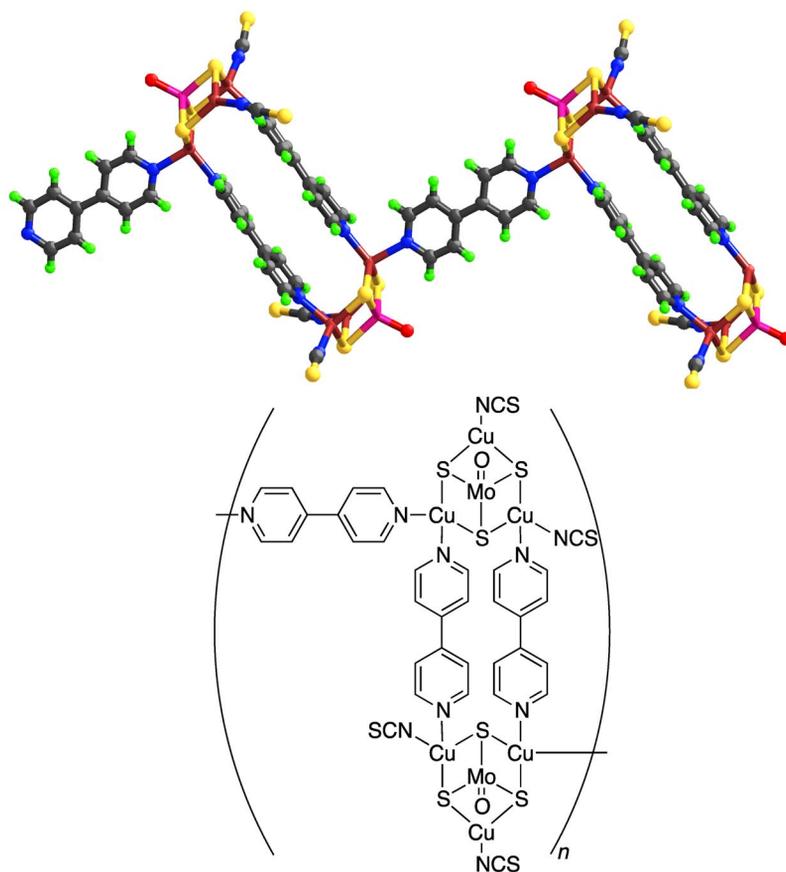


Fig. 3 Example of loops forming a coordination network, the ammonium cations and the aniline lattice molecules are not shown [11]. Mauve: Mo; brown: Cu; blue: N; grey: C; red: O; green: H.

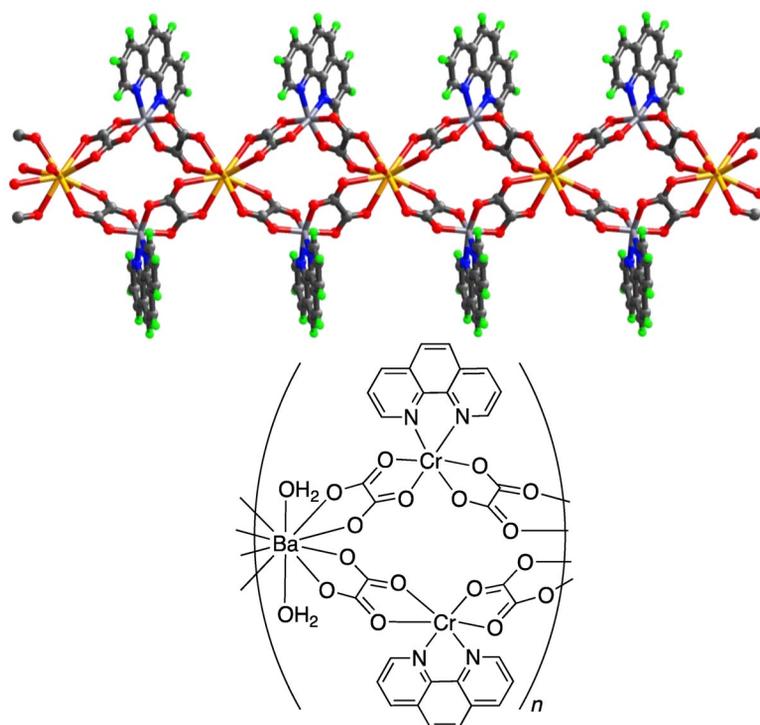


Fig. 4 Example of spiro connections forming a coordination network, the lattice water molecules are not shown [12]. Light grey: Cr; yellow: Ba; blue: N; grey: C; red: O; green: H.

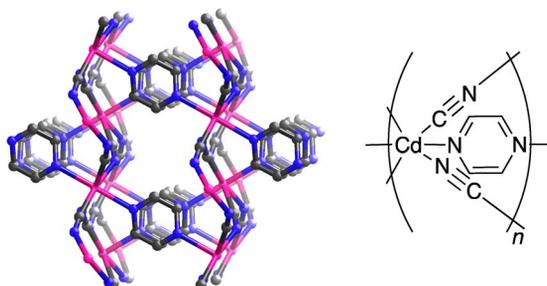


Fig. 5 Example of a coordination network that is also a 3D-coordination polymer from the group of Robson [13]. Hydrogen atoms have been omitted for clarity. Mauve: Cd; blue: N; grey: C.

Metal–organic framework (MOF)

Definition

A metal–organic framework, abbreviated to MOF, is a coordination network with organic ligands containing potential voids.

Comment

This wording accounts for the fact that many systems are dynamic, and changes in structure and thus corresponding changes in potential porosity or solvent and/or guest filled voids may occur depending on temperature, pressure, or other external stimuli. For these reasons it is also not required that an MOF be crystalline. Arguments based on both theory and experiment can be used, suggesting that some of

these coordination polymers (i.e., those that can be described as salts) with direct anion-cation binding are more prone to form structures with open frameworks exhibiting permanent porosity than those forming positively charged networks. However, the grey zone between these extremes is large and increasing so that a definition based on such a charge distinction would be too restrictive.

Moreover, the present definition of MOFs comes very close to a self-definition as the words “metal”, “organic”, and “framework” can be understood and more or less correctly interpreted by a more general scientific audience. This is important as this term is gaining prominence also outside the inorganic chemistry community.

We are aware that a small minority of researchers subscribes to one of two mutually excluding views: either that the term MOF should be exclusively applied to carboxylates or that the term MOF is superfluous and should not be used at all. While these points could have been credibly argued some 10 years ago common practice in the thousands of scientific articles published since has clearly superseded such hard-line distinctions [8].

Examples

An early example of a compound not initially considered as being an MOF is shown in Fig. 6 presented without acetonitrile, acetone solvent, and anions [14].

In Fig. 7 we show two archetypal MOFs: MOF-5 (from the Yaghi group) [15] and HKUST-1 [16].

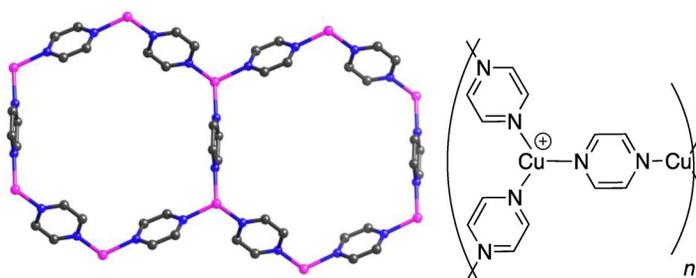


Fig. 6 Example of a coordination network from the group of Kitagawa that can be seen both as a 2D-coordination polymer and as an MOF [14]. Coordinated acetonitrile, acetone solvent, anions (PF_6^-), and hydrogen atoms are not shown. Mauve: Cu; blue: N; grey: C.

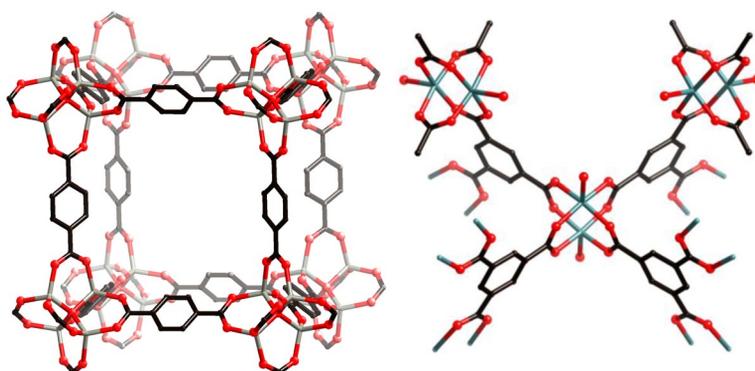


Fig. 7 Archetypal MOFs: Left: The zinc and carboxylate-based MOF-5 from the group of Yaghi where each $[\text{Zn}_4\text{O}]$ unit is bridged by six benzene-1,4-dicarboxylates [15]. Right: HKUST-1 with copper(II) paddlewheel dimers bridged by benzene-1,3,5-tricarboxylates [16]. Hydrogen atoms are not shown. A line drawing is not included for these compounds as the parenthesis and “*n*” convention, as used in previous cases, showing the propagation of the polymer is not workable for these compounds. Light grey: Zn; turquoise: Cu; grey: C; red: O.

RECOMMENDATIONS ON NET AND NETWORK TOPOLOGY

Recommendation

The use of topology and topology descriptors to enhance the description of crystal structures of MOFs and 3D-coordination polymers is strongly recommended. As there are yet no set rules or recommendations available, neither from IUPAC nor from any other relevant international body such as the International Union of Crystallography (IUCr), it is important therefore that the utmost clarity, unambiguity, and transparency are used when presenting these topologies in a scientific article.

Comment

The basis for this recommendation is that the use of topology is an efficient tool for the understanding of the often 3D extended structures of coordination polymers and MOFs. Once such network analysis has been performed it is also easier to compare materials from different publications as, for example, two MOFs having the same net topology does not imply that they are isomorphous or isostructural. Accurate and careful use of network topologies will make scientific communication more efficient.

RECOMMENDATIONS ON TOPOLOGY DESCRIPTORS

Recommendation

Detailed recommendations on the use of topology descriptors cannot be made at the present time, but adherence to the advice in the comment below is recommended at present.

Comment

The use of the symbols or codes in the Reticular Chemistry Structural Resource (RCSR) database is encouraged [17]. As this database does not yet have a permanent hosting with an international body committed to its long-term upkeep, it is not possible at the present time to give this as a firm IUPAC recommendation. For the more general topology terms such as point symbols it is recommended that the advice outlined by an ad hoc assembled group of scientist from the USA, Russia, and Italy [18] is followed.

Examples

The topology descriptors in the RCSR are composed of three letters, occasionally with a fourth letter after a hyphen. The topology of the structure in Fig. 5 is within this system called **rob**, and MOF-5 in Fig. 7 has the **pcu** topology, and HKUST-1 forms a **tbo** net. The 2D topology of Fig. 6 is named **hcb**.

RECOMMENDATIONS ON THE USE OF OTHER TERMS

Recommendation

IUPAC should not at the present time endorse any other terms in the area. The only term that is explicitly discouraged is “hybrid organic–inorganic materials”.

Comment

The task group is aware of and has extensively investigated and probed the scientific community on the appropriate use and utility of the many other terms currently found in the scientific literature. The view of the group is that a simple prefix to the endorsed terms “coordination polymer” and “metal–organic framework” can easily and more efficiently communicate any further specification needed. Such specification typically would indicate properties, such as in porous coordination polymers, constituents such as carboxylate-MOF, or network topology, such as dia-MOF, such terms not being mutually excluding, but rather used as the authors see fit to emphasize different aspects of their materials.

The term “hybrid inorganic–organic material” is sometimes used for MOFs but the task group finds this description imprecise. The term “hybrid material” is mainly used in sol-gel processing and ceramization and clearly is meant to describe materials with distinct components, the definition being “material composed of an intimate mixture of inorganic components, organic components, or both types of component.” In the IUPAC recommendations it is noted that “The components usually interpenetrate on scales of less than 1 μm ” [19]. The appropriate use of the term in the context of MOFs needs to have the complete wording: “chemically bonded hybrid inorganic–organic coordination polymer”. However, one should then be aware that most coordination compounds made over the last 50 years could in a similar way be termed as “hybrid inorganic–organic”, a classification that does not seem to add any value.

RECOMMENDATIONS ON NOMENCLATURE

Recommendation

A task group is currently revising the IUPAC 1984 recommendations [20] for the nomenclature of coordination and inorganic polymers. We note that for the compounds in this article proper IUPAC-endorsed names cannot be given.

Comment

It is clear that whatever the outcome of these coming new recommendations, the use of an IUPAC-endorsed name in a flowing text will be cumbersome (although essential to include). The present task group can agree with the common practice of giving important new compounds trivial names or nicknames based on their place of origin followed by a number such as HKUST-1, MIL-101, and NOTT-112.

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Membership of the task group Coordination Polymers and Metal–Organic Frameworks: Terminology and Nomenclature Guidelines was as follows: **Chair:** L. Öhrström (Sweden); **Members:** S. R. Batten (Australia); N. R. Champness (UK); X.-M. Chen (China); J. García-Martínez (Spain); S. Kitagawa (Kyoto, Japan); M. O’Keefe (USA); M. P. Suh (Korea); J. Reedijk (Netherlands).

The task group held an initial meeting in Glasgow (UK) 2009, an additional smaller meeting in San Juan (Puerto Rico, USA) 2011, and had a final meeting in Stockholm (Sweden) 2012. During the duration of the project the group engaged in intensive E-mail discussions and active interactions with the scientific community. The latter exemplified, but was not restricted to, such activities as:

1. Publishing a discussion paper in the RSC (UK) journal *CrystEngComm* [8], selected as a “hot” paper by the editors and being of the most accessed articles during 2012.
2. Public and by invitation only surveys (announced on the project IUPAC page, the *Dalton* and *CrystEngComm* blogs, the ACS *Crystal Growth & Design* network and the LinkedIn *Metal–Organic Framework* group) receiving almost 100 answers, the essentials of which were reported in the aforementioned *CrystEngComm* article [8].
3. Shorter promotional and informative text presenting the work was published by IUPAC’s news journal *Chemistry International* [21] and in Wiley-VCH’s online magazine *ChemViews*, the latter yielding more than 1400 views.
4. The outcome of the project, essentially this document, was presented as a poster during the International Conference on Coordination Chemistry, ICC 40 in Valencia, Spain, 2012, and as an oral presentation during the 3rd International Conference on Metal–Organic Frameworks and Open Framework Compounds in Edinburgh, UK, 2012.

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