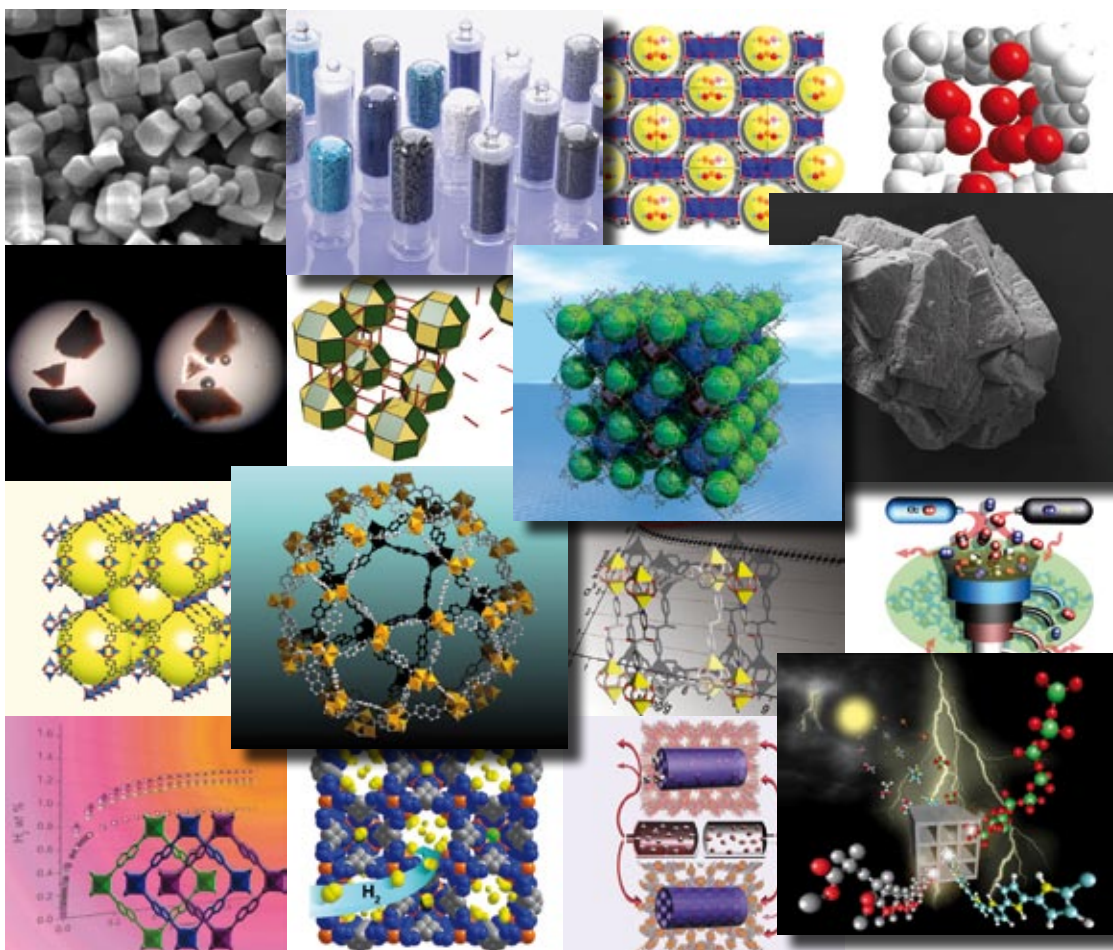# Chem Soc Rev

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Guest Editors Jeffrey Long and Omar Yaghi

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Secondary building units, nets and bonding in the chemistry of metal–organic frameworks†

David J. Tranchemontagne, José L. Mendoza-Cortés, Michael O'Keeffe and Omar M. Yaghi*

This *critical review* presents a comprehensive study of transition-metal carboxylate clusters which may serve as secondary building units (SBUs) towards construction and synthesis of metal–organic frameworks (MOFs). We describe the geometries of 131 SBUs, their connectivity and composition. This contribution presents a comprehensive list of the wide variety of transition-metal carboxylate clusters which may serve as secondary building units (SBUs) in the construction and synthesis of metal–organic frameworks. The SBUs discussed here were obtained from a search of molecules and extended structures archived in the Cambridge Structure Database (CSD, version 5.28, January 2007) which included only crystals containing metal carboxylate linkages (241 references).

Introduction

The chemistry of stitching molecular building units by strong bonds into extended structures (reticular chemistry) continues to develop at an unusually fast pace. This is leading to the proliferation of new structures in which typically metal ion 'joints' are used in connecting organic 'struts' to make porous metal–organic frameworks (MOFs) which we clearly differentiate from coordination polymers. At present, this chemistry has matured to the point where researchers from fields beyond chemistry are involved in the design and study of MOF structures and their properties. Naturally, as in any other mature field, a system of organization and nomenclature should be

developed to facilitate the navigation within the field for current and future researchers. In this context, the concept of secondary building units (SBUs) has served as an organizing concept for the classification of the MOF structures into their underlying topology. SBUs are essential to the design of directionality for the construction of MOFs and to the achievement of robust frameworks. In this contribution we (1) provide a comprehensive list of SBUs that are known as discrete metal carboxylates and that are potentially useful in the construction of MOFs, (2) identify and describe their underlying geometry, (3) discuss the general classification of the nets of MOF structures, and (4) present a unified view of the bonding within MOFs based on SBUs and compare it to coordination polymers.

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Nets and their symbols

Since the earliest days of crystallography crystal structures have been described in terms of *nets* in which atoms are the

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vertices and the bonds are the links (*edges*) between them. The structure of diamond should be a familiar example. These nets are special kinds of periodic graph.[1] In structures such as those of zeolites,[2] tetrahedrally-coordinated atoms T (typically Si, Al, P *etc.*) are joined by –O– links to form a four-coordinated net of T vertices with the –O– links now acting as edges.

Much of the early interest in nets developed particularly with the study of coordination polymers beginning some 75 years ago. In coordination polymers typically a transition-metal (M) ion is linked by a polytopic coordinating ligand such as bipyridine (BPY) to form salts with charged continuous periodic frameworks M(BPY)$_2$. The underlying topology of the structure is again described by a periodic net in which atoms are the vertices, but now the edges correspond to the linkers joining the two edges (BPY in this example). References to some early examples of these materials have been given elsewhere.[3]‡

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‡ At the suggestion of a referee we elaborate on the remarks of the previous paragraph. First the bond energy for four Zn–O bonds in ZnO is determined from the heat of reaction for $ZnO_{(c)} \rightarrow Zn_{(g)} + O_{(g)}$ calculated to be 725.3 kJ mol^{-1} for four Zn–O bonds of bond valence 1/2 (here, as usual, c and g refer to crystalline and gas states). This in turn is determined from the standard heats of formation in kJ mol^{-1} of $ZnO_{(c)}$ (−348.3), $Zn_{(g)}$ (130.2), and $O_{(g)}$ (246.8).[239] We note that a study of bond energies in solid oxides showed that, per mol of O, bond energies to a given metal were closely constant for a variety of ternary, quaternary, *etc.* compounds and did not depend on coordination number (thus for one Mg forming four or six or eight bonds to oxygen to total bond energy is the same; *i.e.* bond energy scales with bond valence).[240] Thus first: we expect the Zn–O bond energy in ZnO to be very similar to that in zinc acetate or in MOF-5 so that for the two Zn–O links to each acetate group to be about 360 kJ mol^{-1}. Second we expect for a coordination link with formal bond valence equal to zero to be rather weaker. To estimate these energies we use the enthalpies of reactions such as $ZnCl_2 \cdot 4NH_3 \rightarrow ZnCl_2 + 4NH_3$, found to be 609.6 kJ mol^{-1} from the heats of formation of $ZnCl_2$ (−415.0), NH_3 (38.9) and $ZnCl_2 \cdot 4NH_3$ (−869.0). Other thermochemical data lead to similar results. Mass spectroscopic data reported by Rogers and Armentrout for $M(NH_3)_4^+ \rightarrow M^+ + 4NH_3$ yield 399–472 kJ mol^{-1} for M = 3d transition elements (see their Table 5).[241] We include in our table a comparison between MOF-5 and the coordination polymer $Zn(L)_2(ClO_4)_2$ (L = N,N'-bis(4-pyridyl)urea) to illustrate out point.[3] In both cases, tetrahedrally coordinated Zn are connected by ditopic links to form 3D networks.

The last decade has seen an explosive increase in synthesis and characterization of crystalline materials with frameworks in which building blocks are joined by covalent bonds. Most notable are MOFs in which typically polyatomic inorganic metal-containing clusters are linked by polytopic chelating linkers. In the archetypical and iconic MOF, MOF-5, OZn$_4$ cationic SBUs are linked by the benzenedicarboxylate (BDC) anion to form a continuous cubic neutral framework of composition $Zn_4O(BDC)_3$.[4] The zinc carboxylate unit has formula $Zn_4O(CO_2)_6$, and the six carboxylate carbons (the *points of extension*) are at the vertices of a regular octahedron. The underlying topology of a MOF framework is also that of a net. In this example the cationic cluster is represented by an octahedral six-coordinated vertex and the edges represent the –(C$_6$H$_4$)– linker. Often a polytopic unit can link metal clusters,[3] thus in MOF-177[5] in which the same OZn$_4$ clusters are linked with 1,3,5-benzenetricaboxylic acid the resulting net is mixed (6,3)-coordination.[5]

We have developed a system of nomenclature for common nets and some of their properties are conveniently accessed through a web-based database known at the Reticular Chemistry Structure Resource (RCSR). This system has recently been described in detail elsewhere;[6] here we are content to note that net topologies are assigned a three-letter symbol in bold lower-case; thus the MOF-5 and MOF-177 topologies have symbols **pcu** and **qom**, respectively. Some derived nets have symbols with extensions, a good example is the so-called *augmented* net in which the vertices of the original net are replaced by a cluster of vertices corresponding to the vertex figure of the original net. Thus in **pcu-a** the original six-coordinated vertices are replaced by an octahedron of vertices. More detail can be found at the cited reference.

Terminology and bonding: MOFs, ZIFs and coordination polymers

We propose that a clear distinction be made between MOFs on the one hand and coordination polymers on the other. We can make the distinction in a very elementary way in terms of

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the formal bond valence used in the sense almost universally accepted in solid state chemistry and the consequent bond energy of the linking bond.[7] The term *coordination compound* originally referred to compounds such as $Co(NH_3)_6Cl_3$ studied by Alfred Werner over 100 years ago. Here the Co–N bond has zero formal bond valence. There is of course a weak bond but such a bond typically has energy of about 100 kJ mol^{-1}.[3] One expects that the energetics of M–N bonds for a transition metal linked to the nitrogen of bipyridine, which is again of zero formal bond valence to be similar. We suggest then that the term *coordination polymer* be restricted to materials in which the framework contains essential links of this sort.‡

In a MOF, such as MOF-5, the Zn–O bond has a formal valence of 1/2 and indeed the energy of the *two* Zn–O bonds acting as a framework link is expected to be close to that of a typical C–C bond.[3]

An essential point is that a MOF such as MOF-5 is the salt of the conjugate base of weak acid and the Zn–O bonding is no different in kind from the Zn–O bonding in, say, $ZnCO_3$ and we think no one would want to refer to $ZnCO_3$ as a coordination polymer. Other differences between a typical MOF and a typical coordination polymer is that the inorganic $Zn_4O(CO_2)_6$ SBU in a MOF is typically a polyatomic group; in a coordination polymer it is typically a single atom. The earlier often imparts enhanced stability to MOFs. Thus to excise the inorganic SBU from MOF-5 one needs to break 12 Zn–O bonds. In contrast in a tetrahedral coordination polymer to remove the metal one needs to break 4 M–L bonds. Usually too the MOF framework is neutral and the interstitial space (pores) can be completely empty; a typical coordination polymer has a charged framework and the pores contain essential counter-ions. We summarize these distinctions in Table 1. Of course there will be examples of intermediate materials which will fit some of the criteria for MOFs and some for coordination polymers, but for the great majority of known materials the distinction will be clear and, we believe, usefully made.

Furthermore we make distinction between coordination polymers and MOFs because it was the latter compounds exemplified by MOF-5 which usually have shown thermal stability, permanent porosity and robustness of their frameworks; attributes that are imparted by strong bonds of metal

Table 1 Some distinctions between a typical MOF (MOF-5) and a typical coordination polymer $[Zn(L)_2(ClO_4)_2]$[3,4]

Property	MOF-5	$Zn(L)_2(ClO_4)_2$[a]
Joint (SBU)	Polyatomic (OZn_4)	Monatomic (Zn)
Framework	Neutral	Charged
Pores	Can be empty	Must contain counterions
Formal bond valence (Zn–O or Zn–N)	1/2	0
Estimated link energy (2Zn–O or Zn–N)/kJ mol^{-1}	363	100–150
Zn–X bond to break to excise SBU	12	4
Estimated energy to excise SBU/kJ mol^{-1}	2200	400–600

[a] L = N,N′-Bis(4-pyridyl)urea.

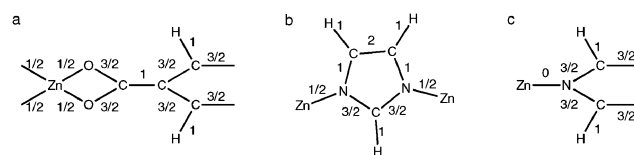carboxylates compared to the coordinate bonds as in Zn bipyridine-type.

Fig. 1 Formal bond valences for (a) tetrahedral zinc bonded to carboxylate oxygen atoms, (b) tetrahedral zinc bonded to nitrogen of imidazolate. (c) Zinc linked to coordinating pyridine. Note that the bond valences must sum to the atom valence (H = 1, Zn = 2, O = 2, N = 3, C = 4). In the cases shown this uniquely determines the bond valences.

ZIFs (zeolitic imidazole frameworks) are special kinds of MOFs that have special properties that justify a special name. Known materials are largely constructed from tetrahedral Zn or Co linked to the nitrogen of imidazolate and again (Fig. 1) the formal valence if the Zn–N bond is 1/2 (just as in Zn_3N_2) and the whole ZIF framework is constructed from strong bonds. The difference in metal–nitrogen bond strength in ZIFs and coordination compounds is illustrated by the exceptional chemical and thermal stability of the former.

SBU Descriptions§

Three points of extension

Three Co atoms are bridged by a central O atom (Fig. 2).[8] Each pair of Co atoms is bridged a carboxylate. Each Co atom is coordinated to a water ligand, and is bridged to a Na atom by a water ligand. The Na atom is coordinated to three water ligands.
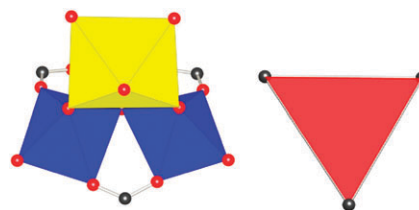

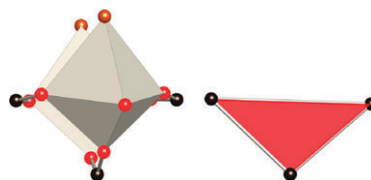**Fig. 2** Triangle:[8] Co, blue; Na, yellow; C, black; O, red.

Fig. 3 Triangle:[9] W, gray; C, black; O, red; Br, brown.

Two W atoms are bridged by three carboxylates (Fig. 3).[9] Each W atom is coordinated to a Br atom and an alkoxy ligand.

§ In this review we generally use names for polyhedra that refer to topology rather than symmetry. Thus an "octahedron" may have less than full octahedral (O_h) symmetry but will be a topological octahedron with four triangular faces meeting at each vertex.
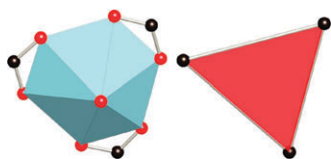
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Fig. 4 Triangle:[10–12] metals (U, Np), blue; C, black; O, red.

A single metal atom is coordinated to three bidentate carboxylates in a triangular arrangement, and two axial O atoms (Fig. 4).[10–12]
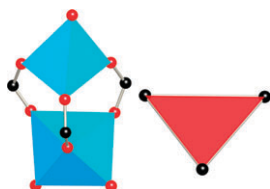

Fig. 5 Triangle:[13] Zn, blue; C, black; O, red.

Two Zn atoms are bridged by three carboxylates (Fig. 5).[13] One Zn atom is coordinated to a single O atom, while the other Zn is coordinated to two O atoms.
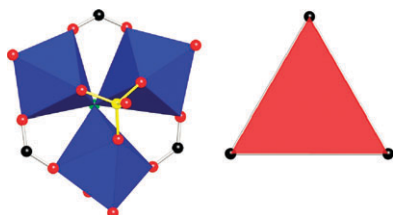

Fig. 6 Triangle:[134] Co, blue; C, black; O, red; S, yellow.

In another triangle SBU, the edges of the triangle are capped with carboxylates (Fig. 6).[14] A sulfate ligand bridges the Co atoms through three O atoms, and each Co atom is coordinated to two O atoms of a diether ligand.
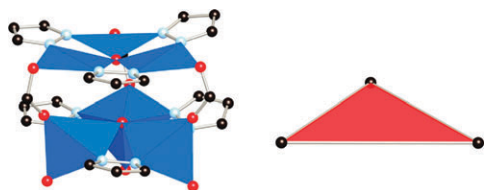
Fig. 7 Triangle:[15] Cu, blue; C, black; O, red.

This SBU is composed of two Cu triangles (Fig. 7).[15] Each triangle is composed of three Cu atoms bridged by central O atoms and three pyrazolate ligands. The two triangles are bridged by three carboxylates, each coordinating in a bismonodentate fashion to a Cu atom of each triangle.
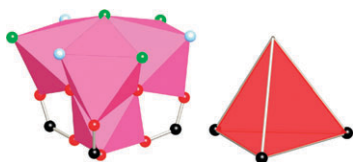
Fig. 8 A triangular SBU:[16] Mn, pink; C, black; O, red; N, blue; Cl, green.

Four Mn atoms are arranged at the vertices of a tetrahedron around a central four-coordinated O atom (Fig. 8).[16] One Mn atom is bridged to each of the other three Mn atoms by a carboxylate. These three Mn atoms are bridged by a three-coordinated Cl atom and are each coordinated to a Cl atom and an amine ligand.
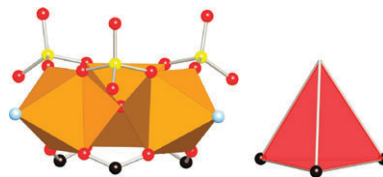
Fig. 9 A triangular SBU:[17] Fe, yellow polyhedra; C, black; O, red; S, yellow spheres.

In this capped Fe(III) acetate cluster, three Fe atoms are arranged at the vertices of a triangle around a central three-coordinated O atom (Fig. 9).[17] Each pair of Fe atoms is bridged by a carboxylate and a sulfate ligand. Each Fe atom is coordinated to an amine capping ligand.
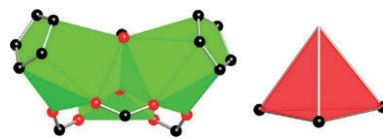

Fig. 10 A triangular SBU:[18–20] metals (Nb, Ti, Zr), green; C, black; O, red.

Three metal atoms are bridged by a central three-coordinated O atom (or hydroxide), which is out of the plane of the metal atoms (Fig. 10).[18–20] Each pair of metal atoms is bridged by a hydroxide and a carboxylate; the carboxylates point outward and downward, giving the SBU pyramidal geometry. Each metal atom is capped by a cyclopentadienyl ligand.
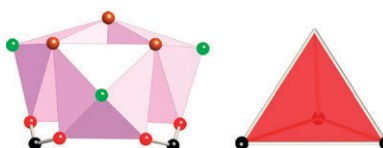

Fig. 11 A triangular SBU:[21,22] Mo, light pink; C, black; O, red; Cl, green; halide, brown.

Three Mo atoms are bridged by a central O atom, which is out of the plane of the Mo atoms (Fig. 11).[21,22] Each pair of Mo atoms is bridged by a halide (Br or Cl) and a carboxylate; the carboxylates point outward and downward, giving the SBU pyramidal geometry. Each Mo atom is capped by a Cl atom.

Four points of extension

Four V atoms are arranged roughly in a square.[23] Each V atom has two water ligands, and is bridged to each of two other V atoms by an hydroxide ligand and by a bridging carboxylate (Fig. 12). The carboxylates are coordinated in a *trans* fashion on each V atom, leading to the overall tetrahedral shape of the SBU.
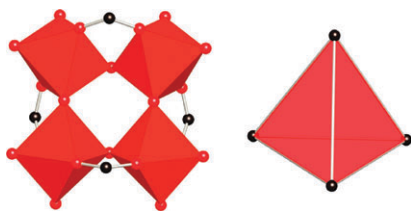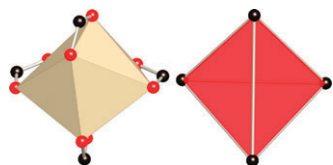
Fig. 12 Tetrahedron:[23] V, red-orange; C, black; O, red.

Fig. 13 Tetrahedron:[24] Ti, tan; C, black; O, red.

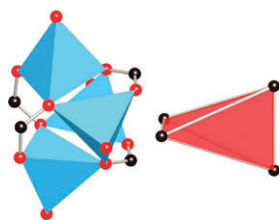A single Ti atom is coordinated by four bidentate carboxylates (Fig. 13).[24]

Fig. 14 Tetrahedron:[25] Li, blue; C, black; O, red.

Four tetrahedral Li atoms are arranged at the vertices of a tetrahedron (Fig. 14).[25] Each Li has a capping alkoxy ligand. Each of four carboxylates bridges three Li atoms, two through an O atom and the third in a monodentate fashion.
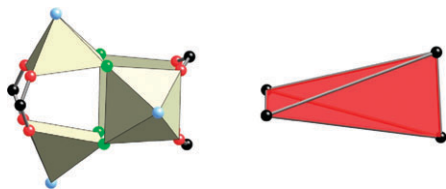

Fig. 15 Tetrahedron:[26] Rh, beige; C, black; O, red, N, blue; Cl, green.

Four Rh atoms are bridged by four Cl atoms to form an elongated tetrahedron, with the Cl atoms capping the four long edges (Fig. 15).[26] Two carboxylates cap each of the two short edges. Four amine ligands coordinate to the four Rh atoms.
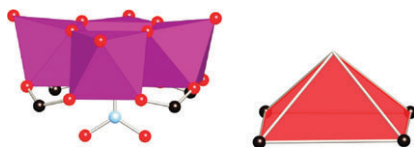
Fig. 16 A rectangular SBU:[27] V, purple; C, black; O, red; N, blue.

Four octahedral V atoms share a nitro ligand as common corner (Fig. 16).[27] Each V atom further shares a bridging O

atom with each of its neighboring V atoms; thus, each octahedron shares one edge with edge neighboring octahedron. A carboxylate bridges each pair of octahedra. The V atoms are each coordinated to an O atom to complete the octahedral coordination. The carboxylates all point downward at an angle, giving the SBU a pyramidal shape.
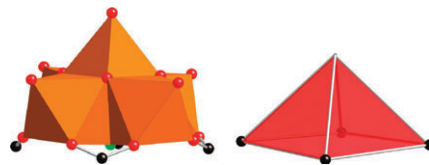

Fig. 17 A rectangular SBU:[28,29] V, orange; C, black; O, red, Cl/Br, green.

A central V atom is bridged to four V atoms through four three-coordinated O atoms (Fig. 17).[28,29] These four V atoms are arranged at the vertices of a square, and each edge is capped with a carboxylate, pointing in a downward fashion to give the SBU a pyramidal shape. The four V atoms are coordinated to a central four-coordinated halide (Cl or Br) atom, and all five V atoms are coordinated to capping O atoms.
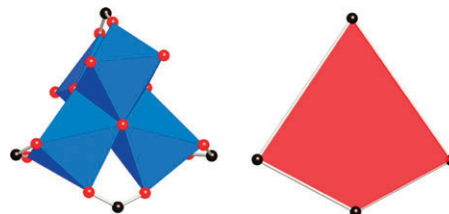

Fig. 18 Kite-shaped quadrilateral:[30,31] metals (Ni, Co), blue; C, black; O, red.

Four octahedrally coordinated metal atoms share edges in a tetrahedron; methoxide ligands serve as the corners of this tetrahedron (Fig. 18).[30,31] Two of the metal atoms are bridged by a carboxylate and are each coordinated to two methoxide ligands. The other two metal atoms are bridged by a carboxylate and are each coordinated by a bidentate carboxylate.
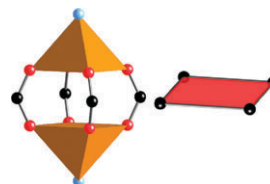

Fig. 19 Square paddle-wheel 1:[32–64] metals (Ru, Cu, Rh, Mo, Fe, Ni, Co, Re, Cr, Zn, Mn, W, Tc, Os, Cd, Bi, Rh/Bi, Pt, Al, Mg, In, Pd/Co, Pd/Mn, Pd/Zn), gold; C, black; O, red; N, blue.

One of the most common SBUs formed by metals and carboxylates is the square paddle-wheel (Fig. 19).[32–64] In this SBU, two metal atoms are bridged by four carboxylates. In most examples, heteroatom containing ligands are bound to the metal ions on the apical positions. This is illustrated by $Cu(CH_3CO_2)_4(C_6H_7N_2)_2$. In some cases, metal–metal bonding may occur, particularly for Mo, W, Os, Tc, Ru; apical ligands

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are not coordinated to the metals in these cases, except in the case of Os. A Ru paddle-wheel is known with observed Ru–Ru bonds and with apical ligands.
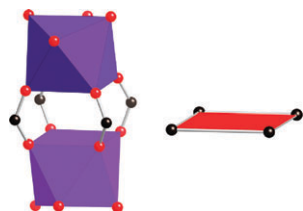

Fig. 20 Square paddle-wheel 2:[65–75] metals (Eu, Tb, Ti, Dy, Sc, Y, Lu, V, Er, Pb, Pr, La, Y, Ba), purple; C, black; O, red.

A second type of square SBU is similar to the first (Fig. 20).[65–75] Two metal ions are bridged by four carboxylates. However, these SBUs are composed of larger metal ions, which can accommodate additional ligands. The known metals of this type, with their capping ligands are:

Eu, with four H_2O per Eu

Tb, with two H_2O and two betaine on each Tb

Ti, Sc, Y, Lu, V, each with Cp ligands

Dy with one trifluoroacetate and three water on each Dy

Sc and Y, each with Cp ligands

Er with mixed capping ligands

Pb with crown ether ligands

Pr with H_2O and trifluoroacetate ligands

La with t-BuCOO ligands capping and bridging the La atoms

Y with pyrazole-containing ligands

Ba with crown ethers
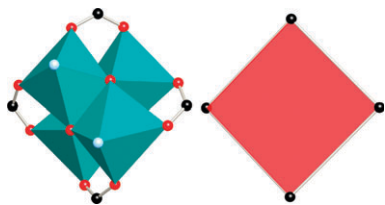
Fig. 21 A rectangular SBU:[76] metals (Co, Ni), aqua; C, black; O, red.

Four metal atoms are arranged at the vertices of a tetrahedron (Fig. 21).[76] The edges are capped by carboxylates, while the faces are capped by three-coordinated O atoms of quinolinol ligands. The N atoms of these ligands coordinate to the metal atoms.
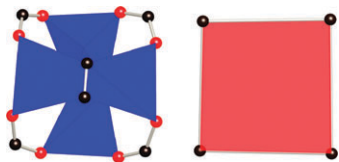

Fig. 22 Distorted rectangular SBU:[77] Cu, blue; C, black; O, red.

Four Cu atoms are arranged at the vertices of a square, with carboxylates capping the edges of the square (Fig. 22).[77] Cu atoms on opposite corners of the square are bridged by bridging η^2-alkyne (3-hexyne) ligands.
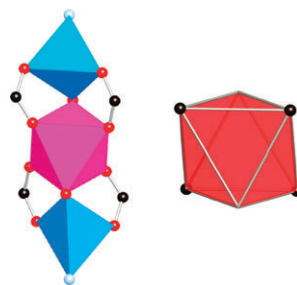

Fig. 23 A rectangular SBU:[78] Zn, blue; metals (Mn, Co, Ni, Cd), pink; C, black; O, red; N, blue.

In some cases similar to the octahedra in Fig. 43 (below), each end metal atom is bridged to the central metal atom by two carboxylates and an oxide-containing ligand (Fig. 23).[78] These SBUs are rectangular, having only four points of extension.
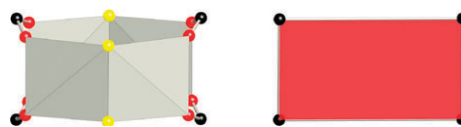

Fig. 24 A series of similar rectangular SBUs:[79–83] Pd, gray; C, black; O, red; S, yellow.

A rectangle is formed by four square Pd atoms in two pairs (Fig. 24).[79] Each pair is bridged by two sulfide ligands, and the two pairs are bridged by the four carboxylates.

Example 2[80] is like Example 1, but each pair is bridged by two CO ligands.

Example 3[81] is like Example 1 but each pair is bridged by one sulfide ligand and one C_6H_4 ligand.

Example 4[82] is like Example 1, but each pair is bridged by two isocyanide ligands.

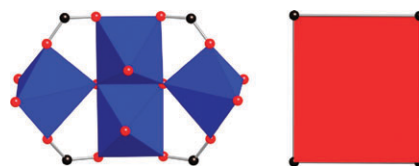Example 5[83] is like Example 1, with Cu atoms and methoxide bridging ligands.

Fig. 25 Rectangle:[84] Cu, blue; C, black; O, red.

Two central Cu atoms are bridged to each other and to the other two Cu atoms by two three-coordinated hydroxides (Fig. 25).[84] The central Cu atoms are also bridged to each of the other Cu atoms by two carboxylates. The central Cu atoms are also bridged to each other by a sulfate ligand. The other two Cu atoms each have two water ligands.
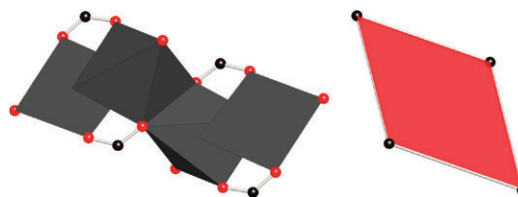

Fig. 26 Parallelogram:[85] Ag, gray; C, black; O, red.

Two Ag dimers each are formed by two bridging carboxylates, and each Ag also has a water ligand (Fig. 26).[85] One carboxylate of each dimer coordinates to a Ag atom of the other dimer through one O atom.
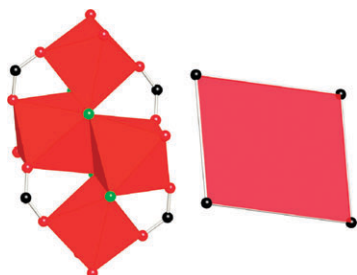

Fig. 27 Parallelogram:[86] V, red-orange; C, black; O, red; Cl, green.

A similar SBU to the parallelogram above has two central V atoms bridged to each other and to the other two V atoms by two three-coordinated Cl atoms (Fig. 27).[86] The central V atoms are bridged to each of the other V atoms by two carboxylate and two bridging Cl atoms. These V atoms each have an alkoxy ligand, while the other two V atoms each have two alkoxy ligands.
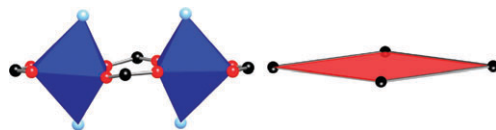

Fig. 28 Parallelograms:[32,87] metals (Co, Ni), blue polyhedra; C, black; O, red; N, blue spheres.

Two metal atoms are each coordinated to a bidentate carboxylate and a *trans*-bidentate capping diamine ligand (Fig. 28).[32,87] The two metal atoms are bridged by two carboxylates.
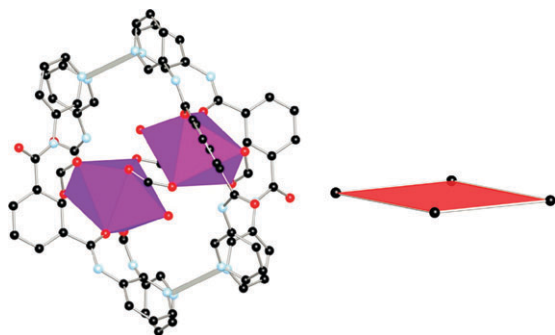

Fig. 29 Parallelogram:[88] Pd, gray; K, purple; C, black; O, red.

Two K atoms are bridged by two carboxylates, and each K atom is also coordinated to a bidentate carboxylate (Fig. 29).[88] Each K is also coordinated to a water ligand and two *m*-bis(pyridylamido)benzene ligands through O atoms. Four pyridyl ligands coordinate to each of two Pd atoms above and below the parallelogram plane.

Five points of extension

A W dimer is capped by two O atoms (ketones), and the two W atoms are bridged by three carboxylates (Fig. 30).[9] Each W atom is coordinated to a bidentate carboxylate.
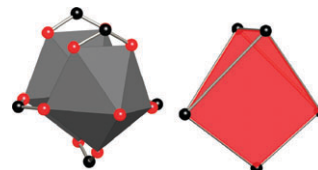

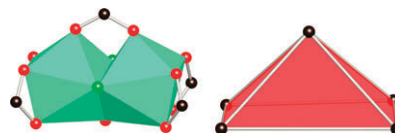**Fig. 30** An SBU with five points of extension:[9] W, gray; C, black; O, red.

Fig. 31 Square pyramid:[89] Nb, green polyhedra; C, black; O, red, Cl, green spheres.

Two Nb atoms are bridged by an alkoxy ligand, two Cl atoms, and a bismonodentate carboxylate (Fig. 31).[89] Each Nb is coordinated to two bidentate carboxylates.
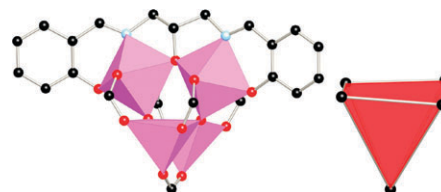

Fig. 32 Square pyramid:[90] Mn, pink; C, black; O, red; N, blue.

Two Mn atoms with square-pyramidal coordination share an edge and are bridged in the apical positions by a carboxylate (Fig. 32).[91] The edge-shared O atoms are also each corners of an octahedral Mn atom. The two remaining corners of the square-pyramidal Mn atoms are occupied by carboxylates that bridge *trans* corners of the octahedral Mn atoms. The octahedral Mn atoms share a central O atom which is part of diaminotrihydroxy ligand; the N atoms and O atoms of this ligand all coordinate to the octahedral Mn atoms.
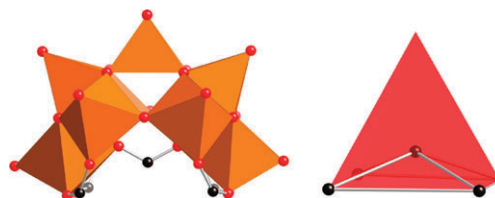

Fig. 33 Square pyramid:[28] V, orange; C, black; O, red.

Nine square-pyramidal V atoms are arranged in a hemispherical manner by edge- and corner-sharing through O atoms (Fig. 33).[28] Five edge-sharing (through O atoms)

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square-pyramidal V atoms are arranged in a curved line. The second and fourth V atoms are each edge-shared to two additional V atoms, which will be denoted as 2′, 2″, 4′, and 4″. V atoms 2′ and 4′ are corner-sharing through an O atom, as are 2″ and 4″. V atom 1 is bridged to 2′ and to 2″ by carboxylates; V atom 5 is bridged to 4′ and 4″ in the same manner. V atoms 1 and 5 are bridged by a central carboxylate, which is pointing downward. All V atoms are capped with O atoms to provide square-pyramidal coordination modes.

Six points of extension

The most commonly found type of trigonal prism consists of three metal octahedra, each coordinated by four bridging carboxylate groups, a central bridging O^{2-} and a heteroatom-containing capping ligand (Fig. 34).[90–100] Thus, there are six carboxylate points of extension. While most examples of this SBU contain one type of metal, several mixed metal examples are known.
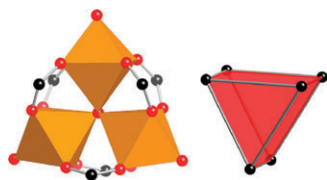

Fig. 34 Trigonal prism type I:[91–111] metals (Fe, Cr, Ru, Mn, V, Ni, Sc, Co, Cr/Co, Ir, Al, Fe/Co, Cr/Fe/Ni, Fe/Zn, Zn, Ga, Fe/Ca), orange; C, black; O, red.
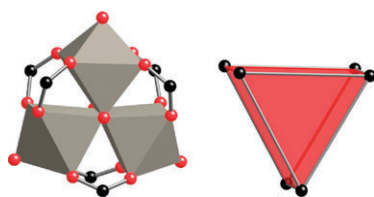

Fig. 35 Trigonal prism type I, variant 1:[112–117] metals (W, Nb, Mo), gray; C, black; O, red.

There are two variations of this type of trigonal prism (Fig. 35).[112–117] In the first variation, there are two three-coordinated O atoms bridging the metals instead of one central three-coordinated O; in one case of this variation (Mo), the metals are bridged by one O^{2-} and an alkyl group.
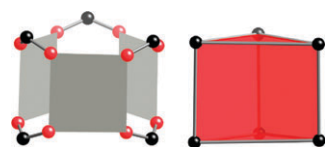

Fig. 36 Trigonal prism type I, variant 2:[117] Pd, gray; C, black; O, red.

The second variation, seen with palladium, consists of square metal atoms and has no capping ligands or central oxygen atoms (Fig. 36).[117]
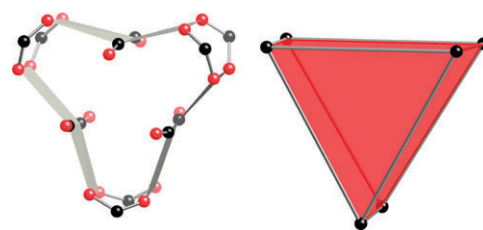

Fig. 37 Trigonal prism:[118–120] metals (Cu, Pd), gray; C, black; O, red.

Additionally, there are other types of trigonal prism (Fig. 37).[118–120] The second type consists of three units of two metals bridged by bridging O-containing groups; these units are connected into a triangular arrangement by six bismonodentate carboxylates, two per corner. This coordination is seen for Pd(II) and Cu(II), with square metal ions in each case. In the Pd case, the bridging O-containing groups are carbonyls, while in the Cu case, ethoxy groups bridge the copper atoms.
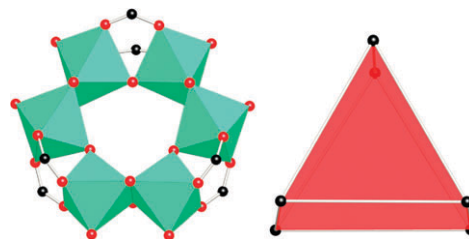

Fig. 38 Trigonal prism:[120] Nb, green; C, black; O, red.

A similar trigonal prism is formed with Nb(IV), wherein the Nb atoms on each side are bridged by ethoxy groups, and each Nb has an ethoxy capping ligand (Fig. 38).[120] Additionally, three O atoms bridge Nb atoms on adjacent sides of the triangle.
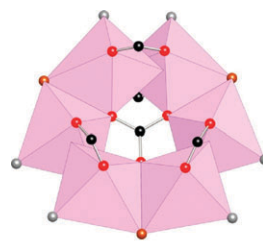

Fig. 39 Trigonal prism:[121] Mo, pink; C, black; O, red; Br, brown; P, gray.

The third type of trigonal prism is seen with Mo (Fig. 39).[121] Each side of the triangle consists of a dimer of square Mo atoms, each with a triphenylphosphine capping group. Two bridging bismonodentate carboxylates arranged *trans* to each other serve as points of extension. A carbonate group at the center of the cluster bridges the three Mo dimers *via* its three bridging O atoms. The apical positions of the Mo dimers are occupied by bromine ions, each bridging two sides of the triangle.
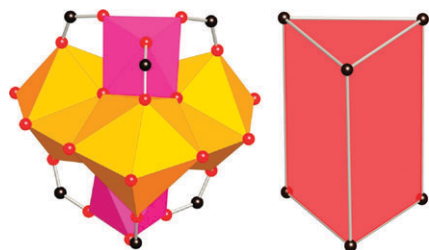
Fig. 40 Trigonal prism:[122] Nd, yellow; Cr, pink; C, black; O, red.

The final trigonal prism is a mixed-metal, Nd/Cr SBU (Fig. 40).[122] The three Nd atoms are arranged at the vertices of a triangle, with the Cr atoms above and below the triangle. Three bridging OH groups connect each octahedral Cr atom to two Nd atoms, as do three bridging carboxylates, the points of extension. Each Nd atom has nine capping water ligands.
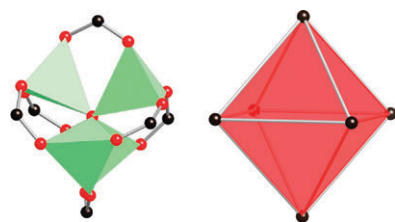

Fig. 41 Octahedra:[123–125] metals (Zn, Co, Be), green; C, black; O, red.

The first type of octahedral SBU has the structure of basic zinc acetate cluster (Fig. 41).[123–125] This consists of a single O atom bonded to four metal atoms to form a M_4O tetrahedron. The edges of the tetrahedron are capped by carboxylates to form the octahedron. This structure has been observed for Zn, Co and Be.
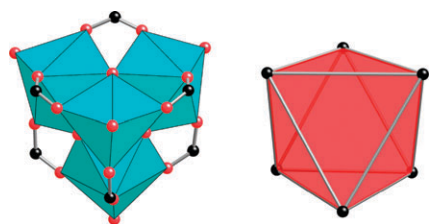

Fig. 42 Octahedra:[126–128] metals (Er, Yb, Nd), blue; C, black; O, red.

A similar SBU is seen for Er, in which four Er are arranged at the vertices of a tetrahedron around a central oxygen (Fig. 42).[126–128] The Er atoms are bridged by three-coordinated O atoms on the faces of the tetrahedron, while the carboxylates caps the edges as in the first type. Three of the Er atoms have two terminal water ligands, while the fourth has one terminal water ligand. The same SBU has been observed for Yb, but in which each Yb has only one capping water ligand, and for Nd, in which the Nd atoms have different numbers of capping water ligands.
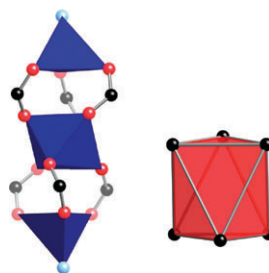

Fig. 43 Octahedra:[129–137] metals (Zn, Co, La/Zn, Mn, Nd/Zn, Ni/Mn, Ca/Zn, Ca/Co, Mg/Zn, Zn/Sr, Mg), blue polyhedra; C, black; O, red; N, blue spheres.

The second type of octahedral SBU consists of two tetrahedral metal atoms and an octahedral metal atom (Fig. 43).[129–137] The two tetrahedral metal atoms are bonded to one capping ligand and three bismonodentate carboxylates, which are also bonded to the central metal atom. These SBUs can contain a single type of metal or two metals with two atoms of metal type 1 bridged to the central metal atom type 2.
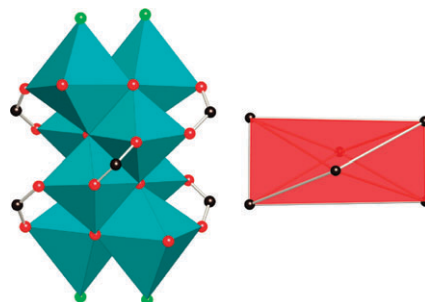

Fig. 44 Octahedron:[138] Co, blue; C, black; O, red; Cl, green.

In a variation, two five-coordinated Zn atoms are capped with ethylenediamine and connected *via* carboxylates to a central seven-coordinated La atom, which is also coordinated to a nitrate ligand. A similar SBU is seen with Zn and Nd.

A rare octahedral SBU is composed of eight Co atoms (Fig. 44).[138] Three face-sharing cuboids with alternating corners of Co and O. The four Co atoms on the ends of the stack are each capped with a Cl atom and an O-containing ligand; all Co atoms have octahedral coordination. Two opposite faces of each cuboid are capped by carboxylates bridging Co atoms diagonally; the carboxylates on each cuboid are perpendicular to each other.
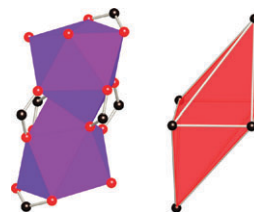

Fig. 45 Octahedron:[139] Tb, purple; C, black; O, red.

An octahedral SBU is formed from two Tb atoms bridged by four carboxylates (Fig. 45). Each Tb has a bidentate carboxylate and two water ligands.[139]
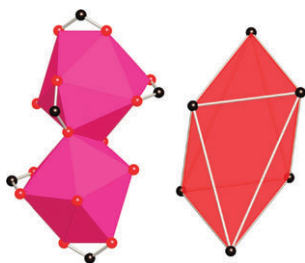
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Fig. 46 Octahedron:[140] Sm, pink; C, black; O, red.

An octahedral SBU is composed of two Sm and six carboxylates (Fig. 46).[140] Each Sm is bonded to two bidentate carboxylates and two water capping ligands. Each of the two remaining carboxylates bridges the Sm atoms through one O atom; the other O atom of the carboxylate is monodentate, bonded to its respective Sm atom.
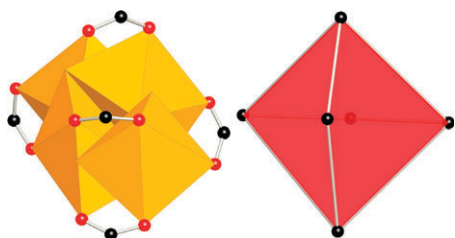

Fig. 47 Octahedron:[141] Ag, yellow; C, black; O, red.

An octahedral SBU has been observed consisting of four Ag atoms arranged at the vertices of a quadrilateral (Fig. 47).[141] Four carboxylates cap the edges of the quadrilateral, each bridging two Ag atoms. The two final carboxylates cap the faces of the quadrilateral. These two carboxylates are perpendicular to each other.
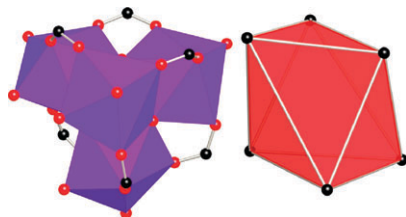

Fig. 48 Octahedron:[142] Tb, purple; C, black; O, red.

In another octahedron, four Tb atoms form a tetrahedron around a central O atom (Fig. 48).[142] The carboxylates cap the edges of the tetrahedron. Four oxide-containing ligands each sit above the faces of the tetrahedron, bridging three Tb atoms. Each Tb has two water ligands.
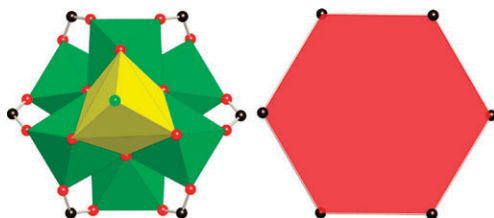

Fig. 49 Hexagon:[143] Ni, green octahedra; Na, yellow; C, black; O, red; Cl, green spheres.

A hexagon SBU is composed of a hexagonal prism with Ni atoms on alternating corners and hydroxides on the remaining corners (Fig. 49).[143] Na atoms are above the hexagonal faces. Carboxylates bridge the Ni atoms. The hydroxides each bridge three Ni atoms to the Na atoms. Six oxide-containing ligands each bridge one Ni atom to one of the Na atoms. The Na atoms are capped with Cl atoms.
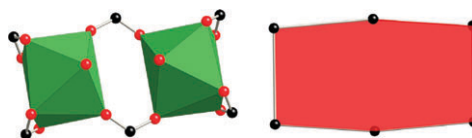

Fig. 50 Hexagon:[144] Er, green; C, black; O, red.

This SBU is composed of two Er atoms and six carboxylates (Fig. 50).[144] Two bidentate carboxylates are bonded to each Er, and two carboxylates bridge the two Er atoms. Each Er has two water ligands.
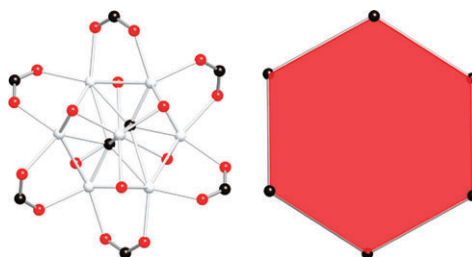
Fig. 51 Hexagon:[145] Ag, white; C, black; O, red.

Eight Ag atoms are in a cube-like arrangement that can also be seen as a hexagon in chair conformation, with a Ag above and below the chair (Fig. 51).[145] The six carboxylates cap the edges of the cube that are also the edges of the chair hexagon, and alkoxy ligands cap the remaining edges of the cube.

Fig. 52 Hexagon:[146] Ti, blue; C, black; O, red.

A hexagonal prism is composed six Ti atoms on alternating corners, six three-coordinated O atoms on the other corners (Fig. 52).[146] Carboxylates bridge the Ti corners, and alkoxide ligands cap the Ti atoms.

Fig. 53 Hexagon:[147] Sn, purple; C, black; O, red.

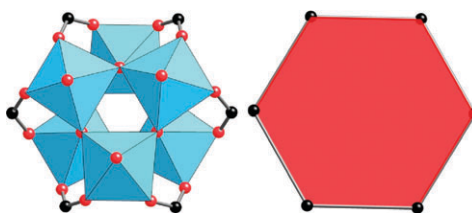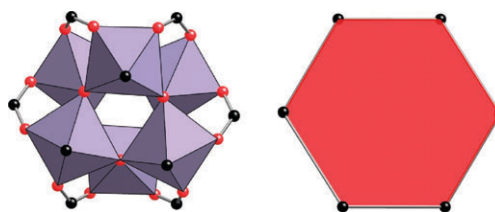Similar to the Ti hexagon above, with Sn atoms (Fig. 53).[147] Each Sn atom has a benzyl ligand completing the octahedral coordination sphere.
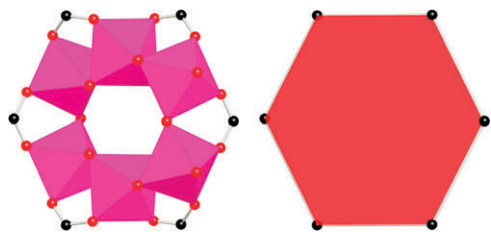

Fig. 54 Hexagon:[148] Cr, pink; C, black; O, red.

Six Cr atoms are arranged at the vertices of a hexagon. Each Cr is octahedral (Fig. 54).[148] It is best viewed as two Cr$_3$ units, in which the central Cr atom is bridged to each of its neighbors by two bridging O atoms and one carboxylate. The two end Cr atoms each have one water ligand. The two Cr$_3$ units are bridged by two bridging O atoms, one per pair of end Cr atoms.
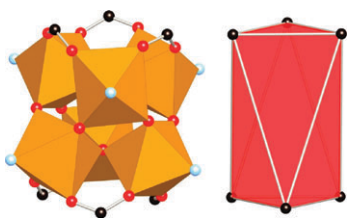

Fig. 55 Trigonal antiprism:[149] Fe, yellow; C, black; O, red; N, blue.

Two triangles are formed, each of three Fe atoms bridged by a central O atom (Fig. 55).[149] Each Fe atom is coordinated to pyridyl ligand, and the sides of the triangle are capped by bridging carboxylates, which point out at an angle from the plane of the Fe atoms. The two triangles are bridged by six O atoms, such that the Fe atoms have corner-sharing octahedral geometry. Thus, the carboxylates of the top triangle point up, and the bottom carboxylates point down and are in a staggered conformation with respect to the top carboxylates.
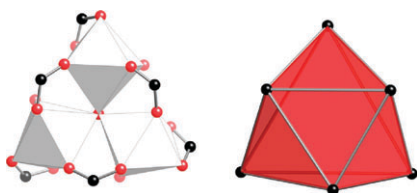

Fig. 56 Distorted trigonal antiprism:[150] Ni, white; C, black; O, red.

Three Ni atoms are arranged at the vertices of a triangle around a central O atom (Fig. 56).[150] Each edge of the triangle is capped by a carboxylate, and each Ni atom is coordinated to an O atom (H$_2$O) and a bidentate carboxylate. This SBU is a distorted version of a trigonal antiprism, in that the opposite faces are of different sizes.
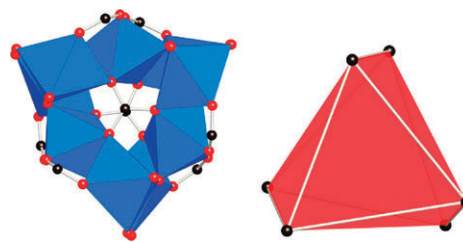

Fig. 57 Twisted trigonal prism:[151] Co, blue; C, black; O, red.

A triangle is formed of nine Co atoms; each corner of the triangle consists of two edge-sharing octahedral Co atoms, and each edge consists of one octahedra Co atom, edge-shared to one Co atom of its respective corner and corner shared to the other (Fig. 57).[151] The edge Co atom is bridged to each corner by a carboxylate such that the points of extension define a twisted trigonal prism. Each corner Co atom is capped by two O atoms, and two carbonate molecules along the C_3 axis provide the O atoms for corner-sharing between the edge Co atoms and the corner Co atoms.
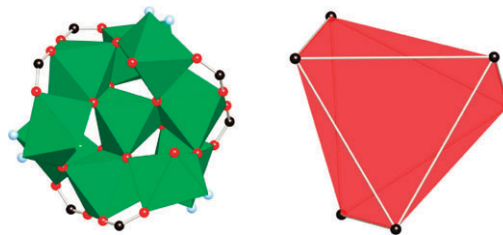
Fig. 58 Twisted trigonal prism:[152] Ni, green; C, black; O, red; N, blue.

This SBU is like the Co SBU described above, but with a central NiO$_6$ unit providing the six O atoms bridging the Ni octahedra, and with six Cl atoms capping each Ni of the "pairs" (Fig. 58).[152]
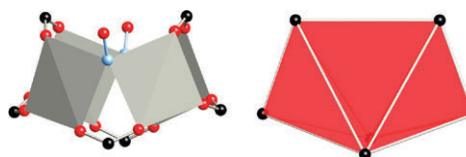
Fig. 59 An SBU with six points of extension:[153,154] metals (Pt, Pd), gray; C, black; O, red; N, blue.

Four square metal atoms are arranged in two pairs, with each pair bridged by an N atom and a carboxylate (Fig. 59).[153,154] The two pairs are close to parallel and are bridged by four carboxylates.

Fig. 60 An SBU with six points of extension:[155] Pt, dark gray; C, black; O, red; N, blue.

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Four Pt atoms are arranged at the vertices of a quadrilateral (Fig. 60).[155] Two opposite edges are capped by four carboxylates, two per edge. Two carboxylates are roughly in the plane of the square, and the other two are roughly orthogonal, both pointing up. The remaining edges are each capped by two N atoms, which are roughly in plane with the square, and two carboxylates, which point down from the plane of the square.
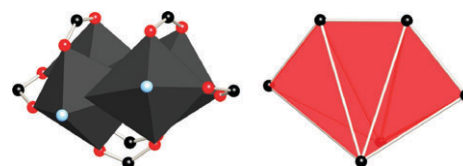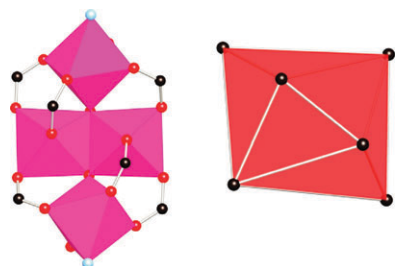

Fig. 61 Six-coordinate SBU:[156] Cr, pink; C, black; O, red; N, blue.

A six-coordinate SBU is known, composed of four Cr atoms and six carboxylates (Fig. 61).[156] Each Cr has octahedral coordination. Two Cr atoms have capping ligands, and each of these two is bridged to a neighboring Cr by three carboxylates and a three-coordinated O, which also bridge the remaining two Cr atoms. These two Cr atoms each have one capping ligand.

Eight points of extension

Eight Pd atoms are arranged at the vertices of two squares (Fig. 62).[157] In each square, the Pd atoms are bridged by NO ligands. The two squares are bridged by eight carboxylates, two per Pd corner.
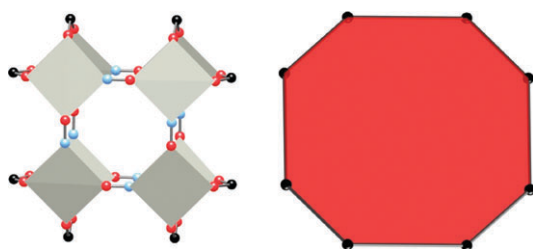
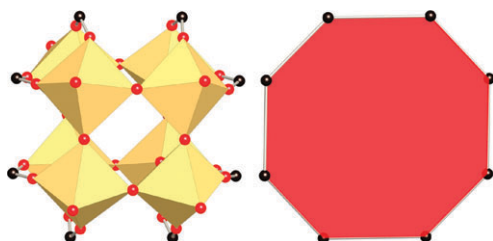

Fig. 62 Octagon:[157] Pd, gray; C, black; O, red; N, blue.

Fig. 63 Octagon:[158] Ta, tan; C, black; O, red.

Eight Ta atoms are arranged at the vertices of a cube (Fig. 63).[158] The Ta atoms of each square are linked by corner-sharing O atoms. The Ta atoms are bridged by eight carboxylates (carbamates), two per Ta corner, and four bridging O atoms, one per corner. Each Ta is capped with a monodentate carbamate.
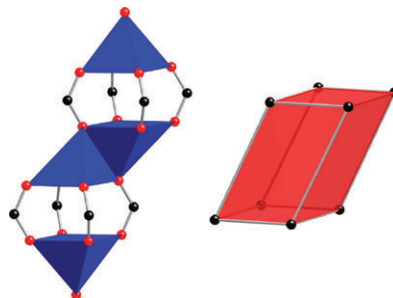
Fig. 64 Rectangular prisms:[159,160] metals (Cu, Rh), blue; C, black; O, red.

Two metal paddle-wheels are connected two each other (Fig. 64).[159,160] An O atom of one carboxylate on each paddle-wheel bridges to a metal atom of the other paddle-wheel, acting as one cap. Each paddle-wheel is also capped by the O atom of a ligand.
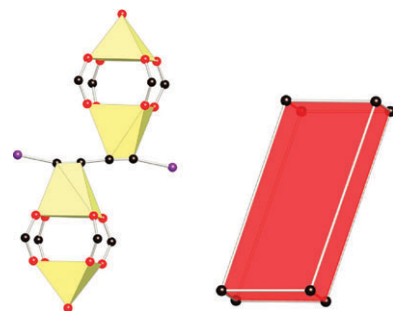
Fig. 65 Rectangular prism:[161] Rh, tan; C, black; O, red; I, purple.

Two Rh square paddle-wheel clusters bridged by 1,4-diiodobuta-1,3-diyne (Fig. 65).[161] Each cluster is coordinated in an η_2 fashion by one of the alkyne units of the butadiyne. Each cluster is capped by a diethyl ether molecule.
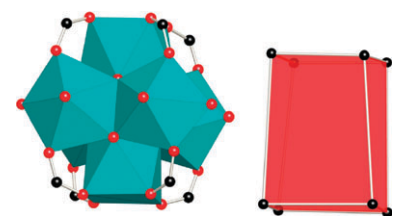
Fig. 66 Distorted rectangular prism:[162] Zn, blue; C, black; O, red.

Six Zr atoms are arranged at the vertices of an octahedron, with μ_3-O atoms capping the faces of the octahedron (Fig. 66).[162] Eight of the edges of the octahedron are capped by carboxylates to yield a rectangular prism SBU. The four equatorial edges are not by capped by carboxylates; instead, each of the four Zr atoms forming those edges is capped by an O atom (hydroxide).
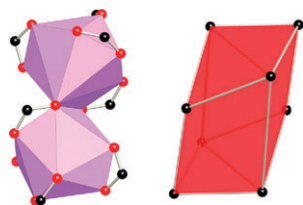
Fig. 67 Distorted rectangular prism:[163] Bi, purple; C, black; O, red; N, blue.

Two Bi atoms are each coordinated in a tetrahedron by four bidentate carboxylates (Fig. 67).[163] One carboxylate on each Bi atom coordinates to the other Bi atom through one O atom.
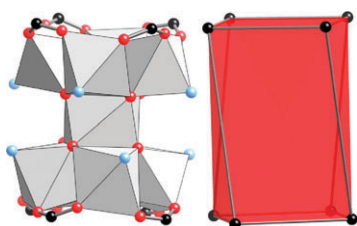
Fig. 68 Twisted rectangular prisms:[164–166] metals (Ni, Fe, Co), white; C, black; O, red; N, blue.

A central Ni is bridged to two sets of four corner-sharing octahedral Ni atoms by eight three-coordinated O atoms; each of these O atoms serves as a shared corner (Fig. 68).[164,165] The four Ni atoms share a central O atom. Eight bismonodentate carboxylates bridge adjacent Ni atoms, and N atoms of amine ligands cap the Ni atoms, completing the octahedral coordination.

The same SBU is seen for Fe, with three-coordinated N atoms bridging the sets of four Fe atoms.[166]
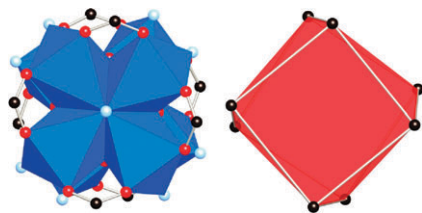

Fig. 69 Twisted rectangular prism:[167] Co, blue octahedra; C, black; O, red; N, blue spheres.

The same SBU is also seen for Co, with a smaller twist around the central Co atom (Fig. 69).[167]
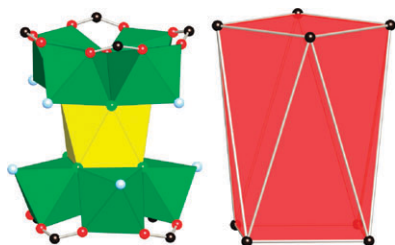
Fig. 70 Square antiprism:[168] Ni, green; Na, yellow; C, black; N, blue.

A square-antiprism SBU is composed in the same manner as the twisted rectangular prism described above (Fig. 70).[168] However, the central Ni is replaced with a Na atom, and three-coordinated F atoms bridge the Na atom to the Ni atoms. The twist is such that the SBU is now a square antiprism.
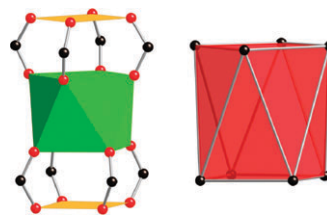
Fig. 71 Square antiprism:[169,170] Au, yellow; Sr, green; C, black; O, red.

Two Au atoms are each bridged to a central Sr atom by four carboxylates, forming two paddle-wheels with a common metal atom (Fig. 71).[169,170] This SBU is also known in which the central atom is Pb.
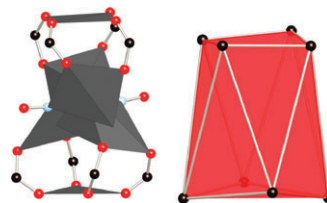
Fig. 72 Square antiprism:[171] Pd, gray; C, black; O, red; N, blue.

Four Pd atoms are arranged at the vertices of a tetrahedron, with bridging NO ligands capping two opposite edges (Fig. 72).[171] Two distorted square Pd atoms are each bridged to the Pd tetrahedron by four carboxylates, two *cis* carboxylates bridging to each corner atom of the tetrahedron.
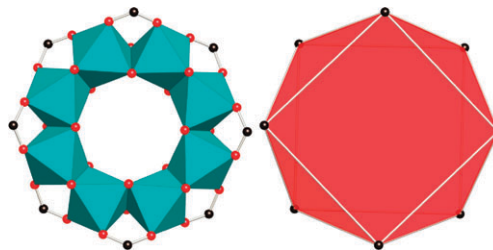
Fig. 73 Square antiprism:[172] Co, blue; C, black; O, red.

This SBU is composed of eight Co atoms and eight carboxylates (Fig. 73).[172] The Co atoms have octahedral coordination; each Co shares one bridging carboxylate and two bridging methoxides with each of its neighboring Co atoms, forming a ring.

Fig. 74 Cube:[173] Cu, blue; C, black; O, red.

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The four Cu atoms are arranged at the vertices of a square around a central hydroxide (Fig. 74).[173] Each Cu atom is bridged to each of two other Cu atoms by two carboxylates (carbonates).
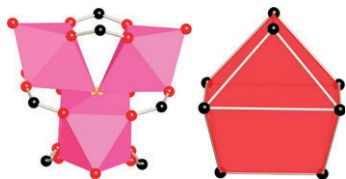
Fig. 75 An SBU with eight points of extension:[174] Cr, pink; C, black; O, red, S, yellow.

Four Cr atoms are arranged at the vertices of a tetrahedron around a central four-coordinated S atom (Fig. 75).[174] Two opposite (perpendicular) edges of the Cr tetrahedron are each capped with two bridging carboxylates. The other four edges are each capped by one bridging carboxylate. Each Cr atom is coordinated to a water ligand.

Fig. 76 An SBU with eight points of extension:[175] Fe, yellow; C, black; O, red; N, blue; P, gray.

In an SBU similar to that in Fig. 86, the carboxylate on the central Fe atom is replaced by a nitro ligand (Fig. 76).[175]
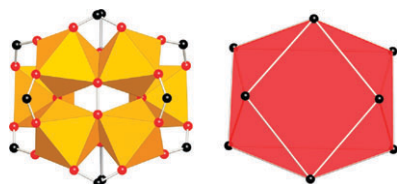
Fig. 77 An SBU with eight points of extension:[175] Fe, yellow; C, black; O, red.
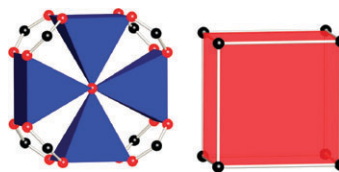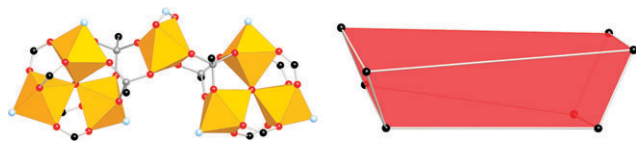
Two Fe_3O triangles are bridged along an edge by an O_2 molecule, forming a rectangle of Fe molecules (Fig. 77).[175] The edges of the triangles and square are capped by carboxylates, eight in total. The remaining edges of the Fe_3O triangle are bridged by PO_3R ligands.
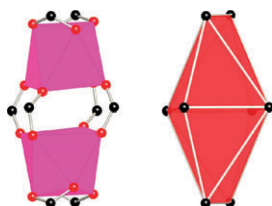
Fig. 78 An SBU with eight points of extension.[176]

Two Eu atoms form a square paddle-wheel with four bridging carboxylates (Fig. 78).[176] Each Eu atom is also coordinated to two bidentate carboxylates, giving eight points of extension total.
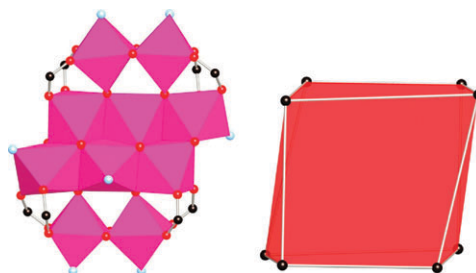
Fig. 79 An SBU with eight points of extension:[177] Mn, pink; C, black; O, red; N, blue.

The core of this SBU is composed of a cluster of six edge-sharing octahedral Mn atoms (Fig. 79).[177] This core is bridged to two pairs of edge-shared Mn octahedra by eight carboxylates, four per pair, and is also corner-shared to the pairs *via* three-coordinated O atoms. Eight 2-hydroxymethylpyridine ligands provide bridging O atoms and capping N atoms.
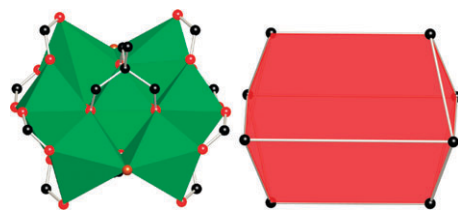
Fig. 80 An SBU with eight points of extension:[178] Ni, green; C, black; O, red.

A central Ni atom is bridged to six Ni atoms arranged at the vertices of a hexagon by two trialkoxy ligands; the three O atoms are all three-coordinated (Fig. 80).[178] Four of the edges of the hexagon are each capped by two carboxylates, while the remaining two opposite edges are capped by Br atoms.
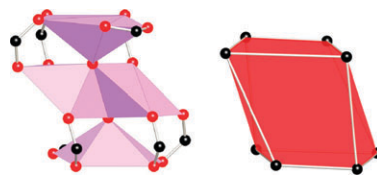
Fig. 81 An SBU with eight points of extension:[179] Bi, purple; C, black; O, red.

Two Bi atoms are each coordinated by a bidentate carboxylate (Fig. 81).[179] They are also each bridged to the remaining central two Bi atoms by one three-coordinated O atom, to one of the two central Bi atoms by one carboxylate, and to the other Bi by two carboxylates. The end Bi atoms each are coordinated to six O atoms, while the central Bi atoms are each coordinated to five O atoms.

Two octahedral Mn atoms share an edge of two three-coordinated O atoms, which are each also coordinated to one Dy atom, one above the Mn atoms and one below (Fig. 82).[180] Each Mn is bridged to each Dy atom by two bismonodentate carboxylates and by one carboxylate through an O atom; these latter carboxylates are bidentate with respect to the Dy atoms. Each Dy has two terminal ligands.
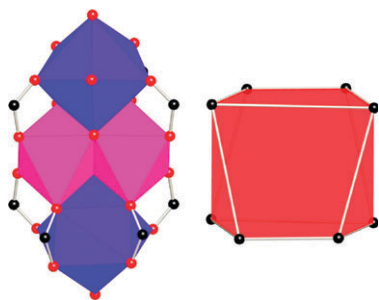
Fig. 82 An SBU with eight points of extension:[180] Mn, pink; Dy, blue; C, black; O, red.
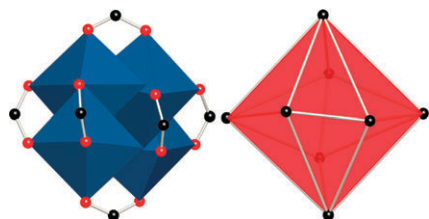
Fig. 83 An SBU with eight points of extension:[181,182] Pt, blue; C, black; O, red.

Four Pt atoms are arranged at the vertices of a square, with carboxylates capping the edges of square (Fig. 83).[181,182] However, two carboxylates occupy each face, each bridging two octahedral Pt atoms. The carboxylates on either face are close to parallel, and the two pairs are close to perpendicular.
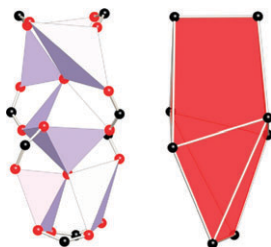
Fig. 84 An SBU with eight points of extension:[183] Sn, white; C, black; O, red.

Two Sn triangles, each with a central O atom, share a central Sn corner (Fig. 84).[183] The edges opposite the central Sn atom are each bridged by two carboxylates. The central Sn atom is bridged to each of the other Sn atoms by a carboxylate.

Nine points of extension

Two Bi atoms and one Al are each coordinated to three carboxylates (Fig. 85).[184] The carboxylates on the second Bi atom each also coordinate to the first Bi atom through one O atom. The three carboxylates on the Al atom each coordinate to the second Bi atom through one O atom.
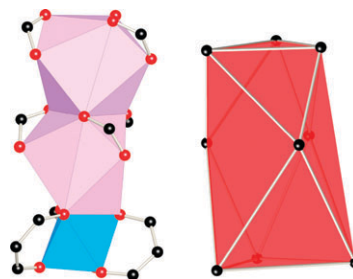
Fig. 85 Face-decorated trigonal prism:[184] Bi, purple; Al, blue; C, black; O, red.
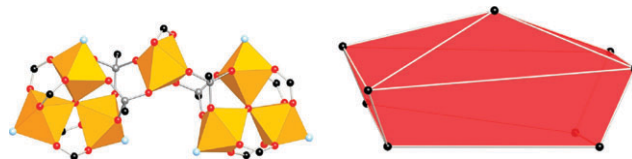
Fig. 86 An SBU with nine points of extension:[176] Fe, yellow; C, black; O, red; N, blue; P, gray.

This SBU is composed of two $Fe_3O(CO_2)_6$ trigonal prisms, with pyridine ligands coordinated to the Fe atoms, in which two carboxylates on one edge of Fe_3O triangle has been replaced by a PO_3R ligand (Fig. 86).[176] The third O atom of each PO_3R bridges each trigonal prism to a central Fe atom. This central Fe atom is also coordinated to a bidentate carboxylate.
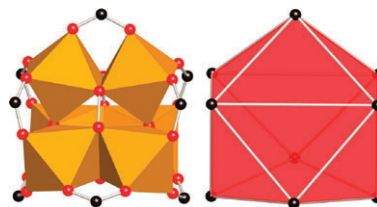
Fig. 87 An SBU with nine points of extension:[185] Fe, yellow; C, black; O, red.

Two triangles are each formed of three Fe atoms bridged by a central O atom (Fig. 87).[185] The edges of each triangle are capped by carboxylates. The two triangles are bridged by three O_2 molecules between parallel edges and by carboxylates at the corners.
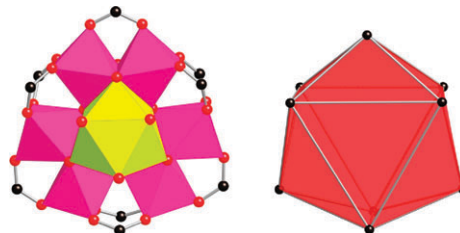
Fig. 88 An SBU with nine points of extension:[186] Mn, pink; Ce, yellow; C, black; O, red.

Three pairs of octahedral Mn atoms, each pair sharing one edge *via* O atoms, forms a triangle; each pair is considered to be a corner of the triangle (Fig. 88).[186] One of the O atoms from each also bridges to a Ce atom. This Ce atom is also

bridged to each Mn atom by a μ_3-O atom, which bridges Mn atoms of adjacent corners. The Ce atom is also coordinated to two water ligands and one methoxy ligand. Each pair of Mn atoms is bridged by a carboxylate, and the three edges of the triangle are each capped by two carboxylates.

Ten points of extension

Two octahedral Mn atoms are bridged by two O atoms to share an edge (Fig. 89).[187] These two O atoms each bridge to two more octahedral Mn atoms as shared corners. Each of the latter pairs of Mn atoms is bridged by a carboxylate, and each Mn of these pairs is bridged to one of the Mn atoms of the former pair by a carboxylate. Additionally, each Mn of the latter pair is bridged to one Mn atom of the former pair and to one Mn of the opposite latter pair by a carboxylate.
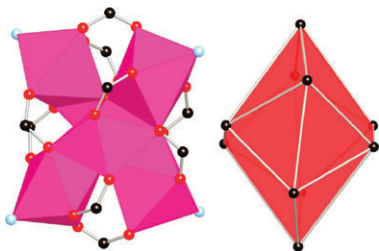
Fig. 89 An SBU with ten points of extension:[187] Mn, pink; C, black; O, red; N, blue.
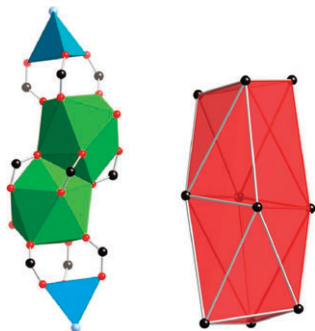
Fig. 90 An SBU with ten points of extension:[188] La, green; Zn, blue tetrahedron; C, black; O, red; N, blue spheres.

Two La atoms are bridged by four carboxylates, and are each coordinated to an alkoxy ligand (Fig. 90).[188] Each La atom is coordinated to a Zn atom by three carboxylates; these Zn atoms are each coordinated to a pyridine ligand.
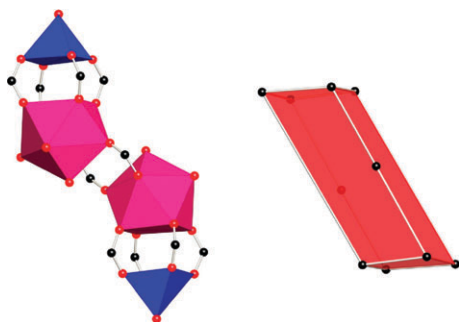
Fig. 91 Rectangular prism with two additional edge points of extension:[189] Cu, blue; metals (Sm, La, Ce, Gd), pink; C, black; O, red.

A water-capped Cu atom is bridged to a metal atom by four carboxylates (Fig. 91).[189] This metal atom has three water ligands. A dimer of bimetal clusters is formed by two bridging carboxylates.
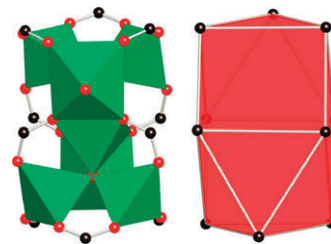
Fig. 92 A rectangular prism with two additional face points of extension:[190] Co, green; C, black; O, red.

Two Co_3O triangles are bridged to a central Co atom through the O atoms and through two carboxylates, each one of which also coordinates to a Co atom of the other triangle (Fig. 92).[190] The edges of each triangle are capped by carboxylates, and one Co atom of each triangle is coordinated to an O atom of trialkylphosphine oxide ligand.
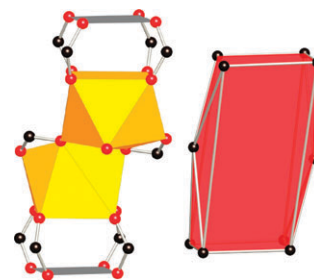
Fig. 93 Rectangular prism with two additional rectangular face points of extension:[100] Pd, gray; metals (Nd, Eu, Ce), yellow; C, black; O, red.

A square Pd atom is bridged to a metal atom by four carboxylates in a paddle-wheel-like fashion (Fig. 93).[100] The metal atom has one water ligand (two for Ce). A dimer of paddle-wheels is formed by two bridging carboxylates; each of these two carboxylates is bidentate to one metal atom and bridges through an O atom.
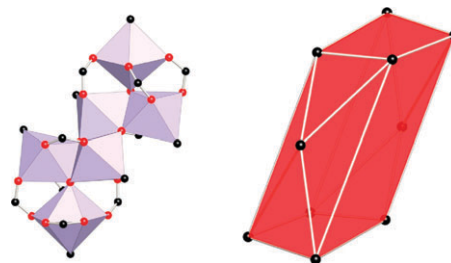
Fig. 94 Rectangular prism with two additional face points of extension:[191] Sn, light purple; C, black; O, red.

Three Sn atoms are bridged by a three-coordinated O atom (Fig. 94).[191] Each Sn atom is coordinated to a benzyl ligand. One Sn atom is coordinated to a bidentate carboxylate and is

bridged to the second Sn atom by one carboxylate, and to the third by two carboxylates. The second and third Sn atoms are bridged by a carboxylate and an O atom. The SBU is a dimer the described Sn cluster, in which the O atom bridging the second and third Sn of one cluster is also bonded to the second Sn atom in the other cluster.
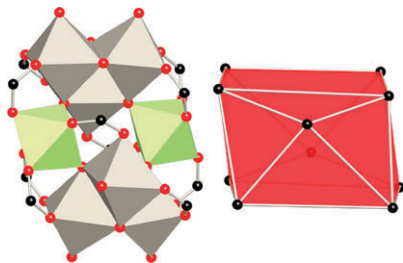
Fig. 95 Rectangular prism with two additional face points of extension:[192] W, gray; Ga, light green; C, black; O, red.

Two sets of three edge-sharing W atoms each share a corner with each of two Ga atoms (Fig. 95).[192] Each Ga atom shares a bridging carboxylate with one W of one trio and two carboxylates with a second W of the same trio, and one carboxylate with a W of the other trio such that each trio is bridged to one Ga by three carboxylates total, and to the Ga by one carboxylate. In each W trio, two of the W atoms are bridged by a carboxylate, and each W atom is coordinated to on O-containing ligand.

The same type of SBU is also seen with V atoms instead of Ga atoms.[193]
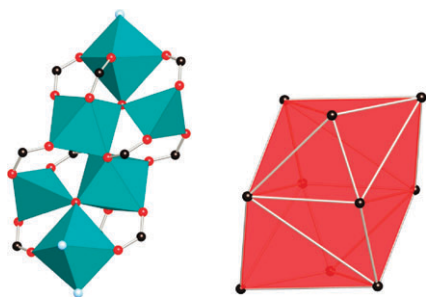
Fig. 96 Rectangular prism with two additional face points of extension:[103] Co, aqua; C, black; O, red; N, blue.

Two Co_3O triangles are bridged by four carboxylates: two of these in a bismonodentate fashion, while two are three-coordinated in one O atom (Fig. 96).[103] This three-coordinated O atom bridges two Co atoms of one triangle to one metal atom of the other triangle. This leaves two sides of each Co_3O triangle, one of which is capped by two carboxylates, while the remaining side of each triangle is capped by one carboxylate. The two "apical" metal atoms (not part of the bridged side) are each coordinated to a pyridine ligand.

A pentagonal antiprism SBU is formed by four Zr atoms arranged at the vertices of a parallelogram (Fig. 97).[194] A three-coordinated O bridges each Zr on the long axis to both of the Zr atoms on the short axis. Each Zr on the long axis is bridged to one Zr on the short axis by two carboxylates, and to the other by three carboxylates, such that all four Zr atoms are
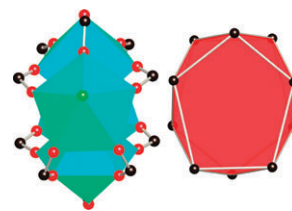
Fig. 97 Pentagonal antiprism:[194] Zn, blue; C, black; O, red; Cl, green.

coordinated to five carboxylates total. The long axis Zr atoms are each coordinated to a Cl atom.
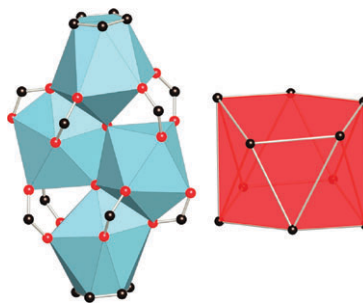
Fig. 98 Distorted pentagonal antiprism:[195] U, light blue; C, black; O, red.

An SBU with similar construction has U atoms instead of Zr atoms and Cp ligands instead of Cl (Fig. 98).[195] Additionally, two of the carboxylates each bridge two Ur atoms differently. These two carboxylates are bridging through one O atom, while the other O atom is monodentate to a U atom along the short axis.
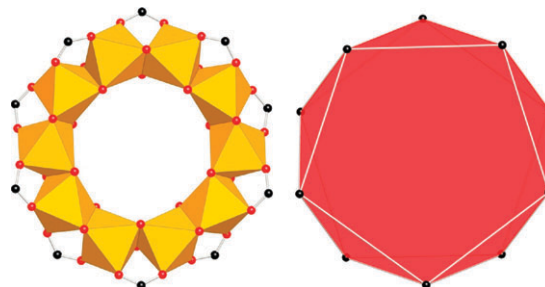
Fig. 99 Pentagonal antiprism:[196–198] metals (V, Fe, Cr), yellow; C, black; O, red.

This SBU is composed of ten metal atoms and ten carboxylates (Fig. 99).[196–198] The metal atoms have octahedral coordination; each metal shares one bridging carboxylate and two bridging methoxides with each of its neighboring metal atoms, forming a ring.

Eleven points of extension

This SBU is formed of six four-coordinate Zr atoms and eight three-coordinate O atoms (Fig. 100).[199,200] Three Zr atoms around each O atom, herein Zr_a, are each coordinated to a bidentate carboxylate. Of the other three Zr atoms, Zr_b, one Zr_b is bridged to each of the other two Zr_b by a carboxylate.

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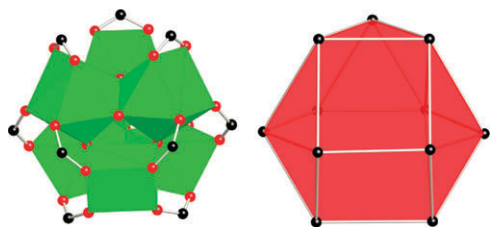
Fig. 100 An SBU with eleven points of extension:[199,200] Zr, green; C, black; O, red.

Each Zr_a is bridged to two Zr_b atoms by carboxylates such that each Zr_b is also bridged to two Zr_a. In total, eleven carboxylates form points of extension.

Twelve points of extension

A cuboctahedron SBU is composed of eight octahedral metal atoms and twelve carboxylates (Fig. 101).[196,201] Each metal octahedron shares three bridging carboxylates and three oxide-based anions with its neighboring metals: one carboxylate and two oxide-anions with the one neighboring metal, and two carboxylates and one oxide anion with the other neighboring metal. In the Fe SBU, each Fe shares one carboxylate and two oxides with the one neighbor, and two carboxylates and a hydroxide with the other neighbor. In the V SBU each V shares one carboxylate and two ethoxides with the first neighbor, and two carboxylates and one hydroxide with the other neighbor.
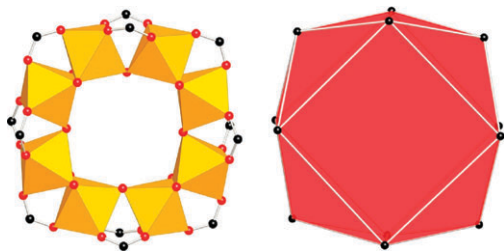
Fig. 101 Cuboctahedron:[196,201] metals (Fe, V), yellow; C, black; O, red.
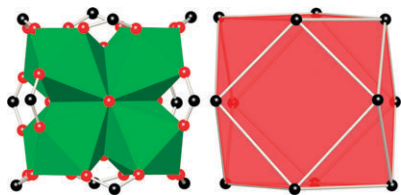
Fig. 102 Cuboctahedron:[202] Ni, green; C, black; O, red.

A topologically equivalent SBU composed of eight Ni atoms and twelve carboxylates is known (Fig. 102).[202] The Ni atoms are arranged at the vertices of a cube. The twelve carboxylates cap the edges of the cube, and six hydroxides each lie above the faces of the cube, bridging four Ni atoms.

This SBU is composed of twelve Fe atoms and twelve carboxylates (Fig. 103).[203] The metal atoms have octahedral coordination; each Fe shares one bridging carboxylate and
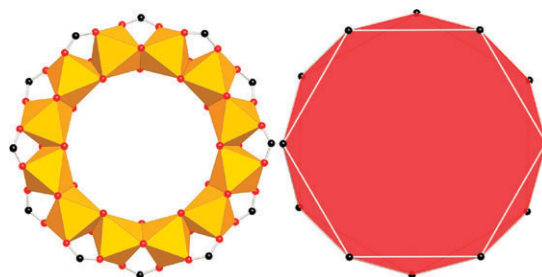
Fig. 103 Hexagonal antiprism:[203] Fe, yellow; C, black; O, red.

two bridging methoxides with each of its neighboring Fe atoms, forming a ring.
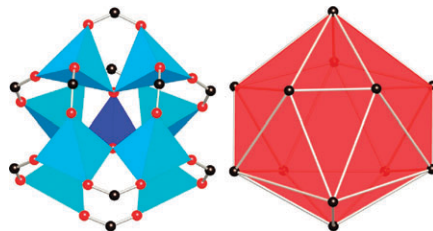
Fig. 104 An icosahedron:[204,205] central metalloid atoms (Si, Ge), dark blue; Zn, light blue; C, black; O, red.

A central tetrahedral metal atom is bridged to eight tetrahedral Zn atoms through four three-coordinated O atoms (Fig. 104).[204,205] The Zn tetrahedra are thus arranged at the vertices of a cube, and the corners of the tetrahedra are bridged to corners of adjacent tetrahedra by carboxylates.
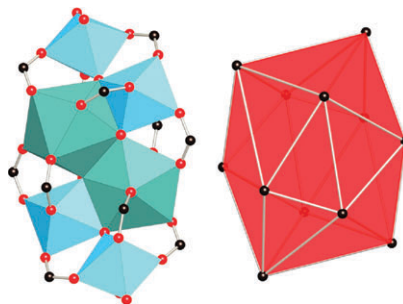
Fig. 105 An icosahedron:[206] Y, aqua; Ti, light blue; C, black; O, red.

Two Y atoms and two pairs of Ti atoms are bridged by four μ_3-O atoms; one O atom bridges each pair of Ti atoms to a Y atom, and the other two O atoms bridge the two Y atoms to on Ti atom from each pair (Fig. 105).[206] Each pair of Ti atoms is bridged by a carboxylate, and one Ti from each pair is capped by two O-containing ligands. Each Y atom is bridged to one Ti from each pair by two carboxylates and to the other Ti atom of each pair by one carboxylate; thus, each Ti atom is coordinated to three carboxylates, and each Y atom is coordinated to five carboxylates.

Four metal atoms are arranged at the vertices of a parallelogram, in which the two metal atoms along the short axis are bridged to each of the other two metal atoms
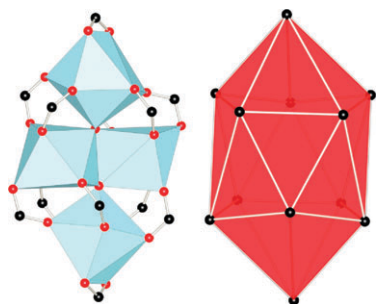
Fig. 106 Icosahedra:[207–209] metals (U, Hf, Zr), light blue; C, black; O, red.

by three-coordinated O atoms (Fig. 106).[207–209] The latter two metal atoms are each coordinated to a bidentate carboxylate, and are bridged to the first two metal atoms by five carboxylates: three to one metal atom, two to the other metal atom, such that all four metal atoms are coordinated to five bridging carboxylates.
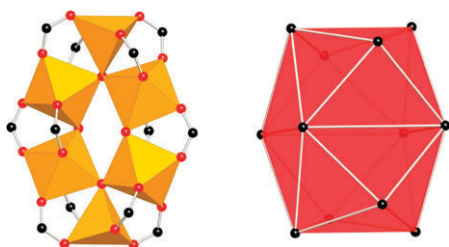
Fig. 107 An icosahedron:[210] Fe, yellow; C, black; O, red.

Two Fe_3O triangles are bridged by two hydroxides and four carboxylates: one hydroxide, and two carboxylates per Fe corner (Fig. 107).[210] This leaves two sides of each Fe_3O triangles, all four of which are capped by two carboxylates. The two "apical" Fe atoms (not part of the bridged side) are each coordinated to an O atom.
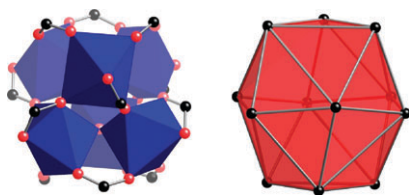
Fig. 108 An icosahedral SBU:[211] Co, blue; C, black; O, red.

Two Co_3O triangles are staggered to each other. The edges of each triangle are capped with carboxylates (Fig. 108).[211] The triangles are bridged by six carboxylates: each carboxylate is bidentate to one Co atom and bridges to one Co of the other triangle through a μ_3-O atom.

Four metal atoms arranged at the vertices of an irregular tetrahedron (Fig. 109).[212–215] Each edge of the tetrahedron is capped by a bridging carboxylate, and each metal atom has a bidentate carboxylate. Each triangular face of the tetrahedron is capped by a carboxylate that is coordinated to one metal atom through one oxygen and bridging two other two metals through the other oxygen.
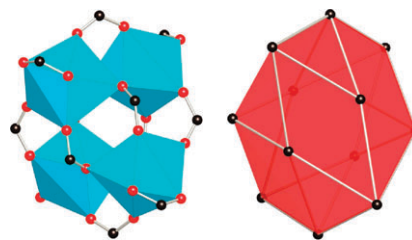
Fig. 109 An SBU with twelve points of extension:[212–215] metals (Sm, Nd, Gd, Ho, Eu, Er, Lu, Yb), blue; C, black; O, red.
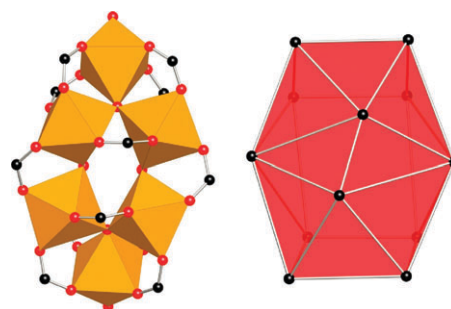
Fig. 110 An SBU with twelve points of extension and seventeen faces:[216] Fe, yellow; C, black; O, red.

A basic Fe actetate cluster has one carboxylate removed and replaced by two O atoms, each bridging to an additional Fe atom (Fig. 110).[216] These latter two Fe atoms are bridged to the basic Fe acetate unit by two carboxylates (one per Fe atom), to each other by a carboxylate, and to a sixth Fe atom by a three-coordinated O atom and four carboxylates (two per Fe atom).
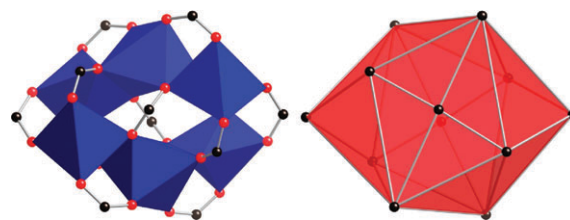
Fig. 111 An SBU with twelve points of extension:[217,218] metals (Co, Mg), blue; C, black; O, red.

Six metal atoms are arranged at the vertices of a hexagon, with each edge capped by a carboxylate (Fig. 111).[217,218] On one side of the hexagon, the first and second metal atoms are bridged by an O atom of a carboxylate, the other O atom of which bridges to the third metal atom. This pattern is repeated with the fourth, fifth and sixth metal atoms. The first and sixth metal atoms share an O atom of a carboxylate, with the third and fourth sharing the other O atom. On the other side of the hexagon, the sharing is seen for the second, third and fourth metal atoms, fifth, sixth and first metal atoms, and first, second, fourth and sixth, respectively.

Two Mn_3O triangles are bridged by four carboxylates: two of these in a bismonodentate fashion, while two are three-coordinated in one O atom (Fig. 112).[219] This three-coordinated O atom bridges two Mn atoms of one triangle to

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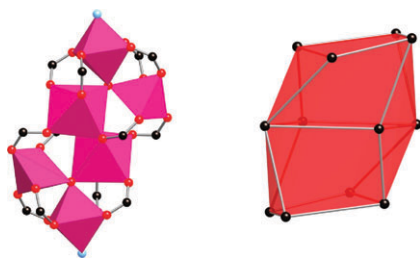
Fig. 112 An SBU with twelve points of extension:[219] Mn, pink; C, black; O, red; N, blue.

one metal atom of the other triangle. This leaves two sides of each Mn_3O triangle, all four of which are capped by two carboxylates. The two "apical" metal atoms (not part of the bridged side) are each coordinated to a pyridine ligand.
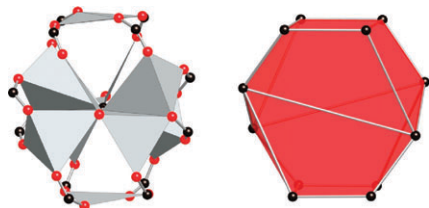
Fig. 113 Distorted hexagonal prism:[145] Ag, light gray; C, black; O, red.

A central acetylene bridges eight Ag atoms, four per C atom (Fig. 113).[145] These eight Ag atoms are arranged at the vertices of two staggered square pyramids, with two Ag atoms from each C atom pointing up to form the base of the top pyramid, and two Ag atoms from each C atom pointing down to form the base of the second pyramid. A ninth and tenth Ag atom each serve as an apex to one pyramid. In each pyramid, the apical Ag atom is bridged to each of the other Ag atoms by a carboxylate. The bases of the two pyramids are bridged by four carboxylates on the long edges. On each end of the acetylene, two close Ag atoms between rectangular bases are bridged by O atoms (alkoxy ligands).
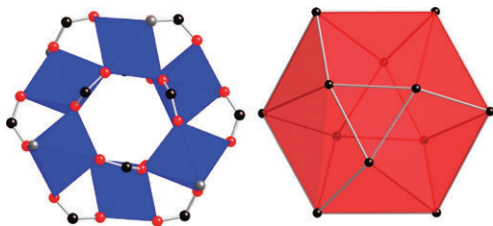
**Fig. 114** A 14-hedron SBU with twelve points of extension:[75,220,221] metals (Ni, Co, Mg, Cu), blue; C, black; O, red.

Six metal atoms are arranged in a chair conformation, with carboxylates capping the edges of the chair (Fig. 114).[75,220,221] Three carboxylates reside above the chair. Each of these carboxylates bridges three metal atoms, two adjacent atoms through one O atom, and the third through the other O atom. This motif if repeated on the other side of the chair with three more carboxylates.
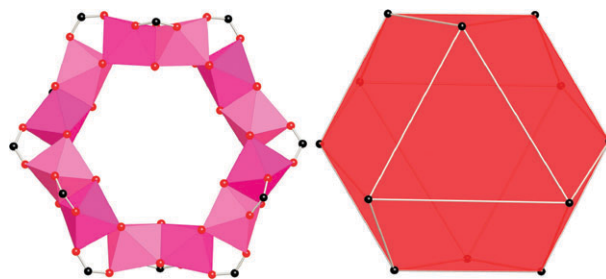
Fig. 115 A 14-hedron SBU with twelve points of extension:[222] Cr/Mn, pink; C, black; O, red.

Six Cr atoms and six Mn atoms are arranged at the vertices of a dodecagon of alternating metals (Fig. 115).[222] Each metal atom shares an edge with each of its neighbors *via* O atoms. The edges of the dodecagon are capped with carboxylates in an alternating up-down fashion.
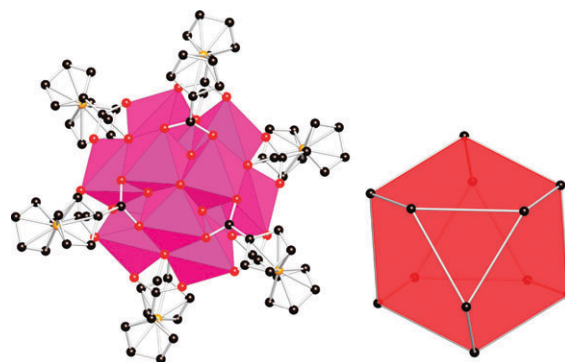
Fig. 116 An SBU with twelve points of extension:[223] Mn, pink; Fe, yellow; C, black; O, red.

A cluster of thirteen Mn atoms and fourteen O atoms in an NaCl lattice is capped by twelve carboxylates of six ferrocene dicarboxylate molecules (Fig. 116).[223]
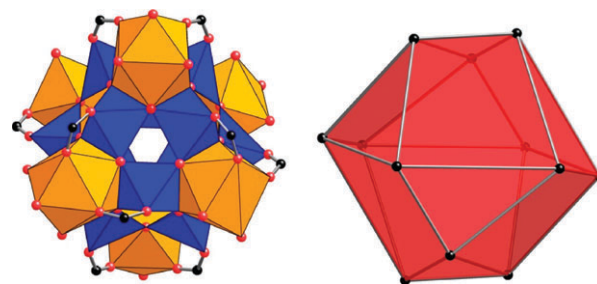
Fig. 117 A 14-hedron SBU with twelve points of extension:[224] Cu, blue; Nd, yellow; C, black; O, red.

A cuboctahedron is formed of twelve Cu atoms (vertices) bridged by 24 O atoms (links/edges) (Fig. 117).[224] Six Nd atoms cap the square faces of the cuboctahedron, inscribing the corners on an imaginary cube. Each Nd is bridged to two Cu atoms by carboxylates and is capped by O-containing ligands.

A cluster of sixteen Ag atoms coordinated around two acetylene ligands capped by twelve carboxylates, two water ligands, and six alkoxy ligands (Fig. 118).[145]
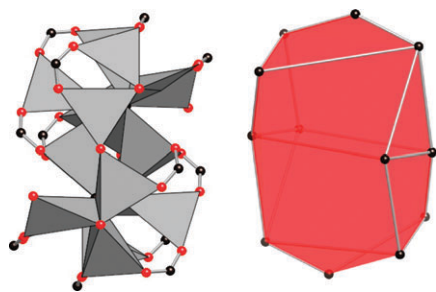
Fig. 118 An SBU with twelve points of extension:[145] Ag, gray; C, black; O, red.
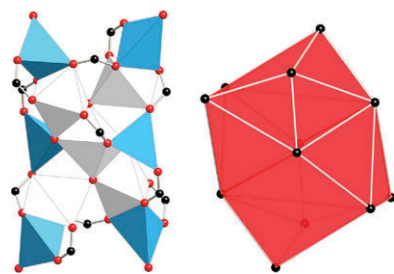
Fig. 119 An SBU with twelve points of extension:[225] Ni, white; Li, blue; C, black; O, red.
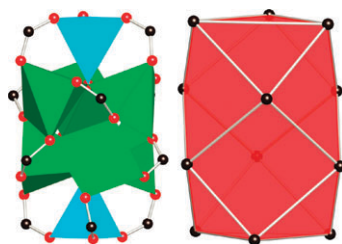
Fig. 120 An SBU with twelve points of extension:[194] Ni, green; Zn, blue; C, black; O, red.

Two Ni_3O triangles share a central Ni atom. The central Ni atom is bridged to the second Ni atom of each triangle by a carboxylate, each of which also bridges the central Ni to a Li atom (Fig. 119).[225] The second and third Ni of each triangle are bridged by a carboxylate, which also bridges each Ni atom a Li atom. The second and third Ni atom of each triangle are also bridged to their respective Li atoms by carboxylates, one of which on each Ni atom bridges back to one of the Li atoms bridged to the central Ni atom.

Two Ni_3O triangles are each bridged to a Zn atom through the central O atom and by three carboxylates, one per Ni atom (Fig. 120).[194] The Ni triangles are bridged by six three-coordinated carboxylates; every Ni atom is five-coordinated.

Fourteen points of extension

Twelve Ag atoms are arranged at the vertices of a central tetrahedron sharing an edge with each of two octahedra (Fig. 121).[226] Note that the Ag atoms of the edges shared between the tetrahedron and the octahedra are too far apart to be bonding (2.96 Å), and are considered edges for convenience of visualizing the structure. The four unshared edges of the
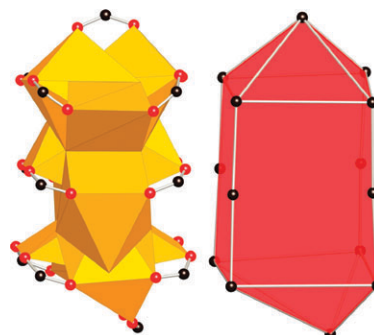
Fig. 121 An SBU with fourteen points of extension:[226] Ag, yellow; C, black; O, red.

tetrahedron are capped with carboxylates. Five of the unshared edges of each octahedron are capped by carboxylates.

In a related SBU, the four bridging atoms are Fe atoms instead of Mn atoms.[179]

Fifteen and sixteen points of extension

A cluster of eleven octahedral Fe atoms and twelve three-coordinated O atoms is capped with fifteen carboxylates, all of which bridge adjacent Fe atoms (Fig. 122).[227] Nine Fe octahedra are arranged in a ring, each sharing an edge with its two neighbors. The remaining two Fe octahedral are only corner sharing, each sharing three corners and coordinated to three carboxylates.
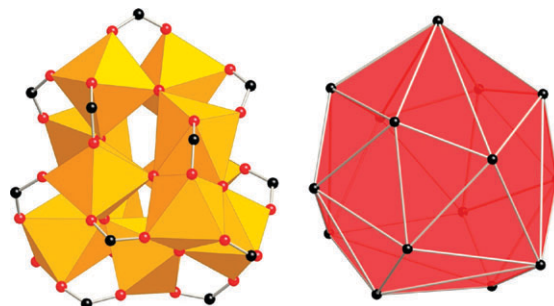
Fig. 122 An SBU with fifteen points of extension:[227] Fe, yellow; C, black; O, red.
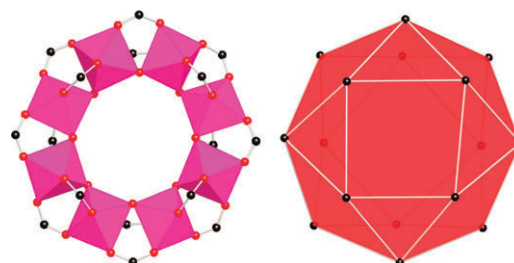
Fig. 123 An SBU with sixteen points of extension:[228–233] metals (Cr, Ti, Zn), pink; C, black; O, red.

This SBU is composed of eight octahedral metal atoms and sixteen carboxylates (Fig. 123).[228–233] Two carboxylates bridge each metal octahedron to each of its two neighboring octahedra, forming a ring of octahedral metal atoms. The remaining

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two corners are occupied by bridging anionic ligands, typically oxide, hydroxide or halide anions. This SBU is known for Cr and Ti, with one example having seven Cr and one Zn.
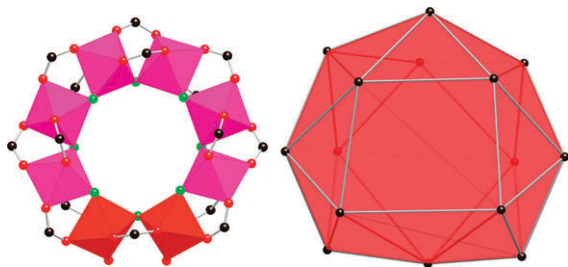
Fig. 124 A variation on the SBU in Fig. 123 with only fifteen points of extension:[229] Cr, pink; V, red-orange; C, black; O, red; F, green.

Two variations of this SBU are known.[229] In the first (Fig. 124), two Cr are replaced with V. These adjacent V octahedra are bridged by only one carboxylate and one fluoride; the remaining corner of each octahedron is occupied by an oxide. This variation has only fifteen carboxylate points of extension.
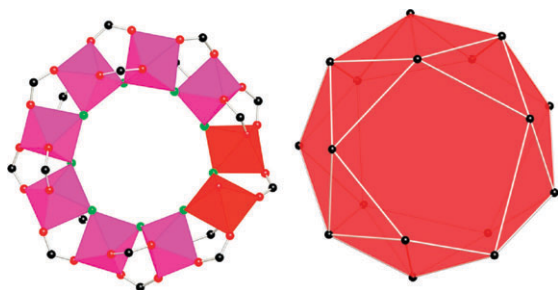
Fig. 125 A second variation of the SBU in Fig. 123:[230] Cr, pink; V, red-orange; C, black; O, red; F, green.

The other variation consists of seven Cr atoms and two V atoms (Fig. 125).[230] Again, the adjacent V octahedra are bridged by only one carboxylate and one fluoride, with oxide ligands on the remaining corner. In this variation, an additional Cr octahedron is incorporated into the ring, connected to its neighbors by two carboxylates; thus, there are seventeen carboxylates.
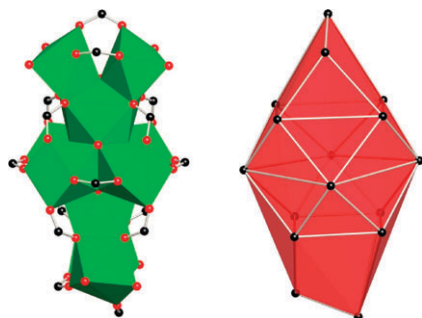
Fig. 126 An SBU with sixteen points of extension:[234] Zr, green; C, black; O, red.

At the center of the SBU lies a rhombic dodecahedron of four-coordinated Zr and three-coordinated O atoms (Fig. 126).[234]

Four faces are capped by carboxylates, each bridging two Zr atoms, forming an "equator". Each of the two Zr atoms at the apexes (with respect to the equator) is bridged to two Zr atoms through a three-coordinated O atom, forming Zr triangles. The farthest four Zr atoms are each capped by O-containing ligands, and the two farthest edges of the triangles are each capped by two carboxylates. The four "equatorial" Zr atoms of the rhombic dodecahedron are bridged to each of the apical Zr atoms by carboxylates, which also bridge to the four triangular Zr atoms, two per triangular Zr atom.
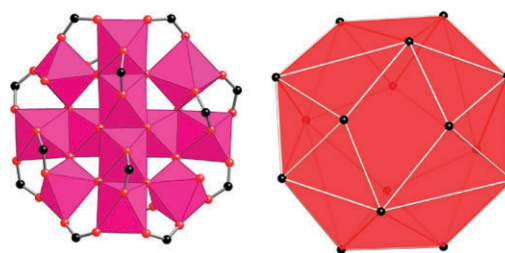
Fig. 127 An SBU with sixteen points of extension:[235] Mn, pink; C, black; O, red.

Eight Mn atoms are arranged in two edge-sharing rows which cross at the centers of the rows, such that a heterocube of Mn and O atoms is formed at the center of the SBU (Fig. 127).[235] In each row, the four Mn atoms are designated into pairs by two bridging carboxylates. The edge-shared O atoms of each pair bridges the pair to another Mn atom, such that four Mn atoms bridge the two crossing rows; these four, along with the four Mn atoms at the ends of the rows form an octagon. Each of these four Mn atoms is bridged to another Mn atom by a carboxylate, and each edge of the octagonal is capped by a carboxylate.

Eighteen points of extension

Sixteen Ag atoms are arranged at the vertices of four square layers around two acetylene units, two outer layers and two inner layers (Fig. 128).[236] One carbon from each acetylene is coordinated to four outer layer Ag atoms, while the other carbon of each acetylene is coordinated to four Ag atoms of an inner and one Ag of the opposite inner layer. Two carboxylates bridge each pair of outer layer Ag atoms. Each set of outer layer Ag atoms is bridged to its closest set of inner layer Ag atoms by six carboxylates, and two inner layer Ag atoms each are bridged to an opposite inner layer Ag atom by a carboxylate.
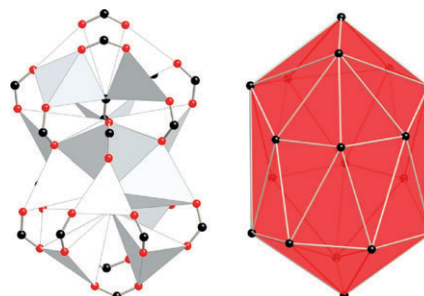
Fig. 128 An SBU with eighteen points of extension:[236] Ag, white; C, black; O, red.
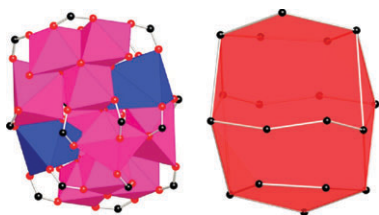
Fig. 129 An SBU with eighteen points of extension:[237] Mn, pink; Ca, blue; C, black; O, red.

A cluster of thirteen Mn atoms and two Ca atoms, sharing edges and corners *via* O atoms, is capped by eighteen carboxylates (Fig. 129).[237]

Twenty-two points of extension

This SBU consists to two semicircles, each of four octahedral Cr atoms and one square-pyramidal Cu atom, corner-shared *via* Cl atoms; these semicircles are joined at each end by an octahedral Cr atom with similar corner sharing (Fig. 130).[229] Each Cu atom is located at one end of its respective semicircle. The two Cr atoms joining the semicircles are bridged to a Cu atom by one carboxylate and to another Cr by two carboxylates. All other metal atoms are bridged to their neighbors by two carboxylates.
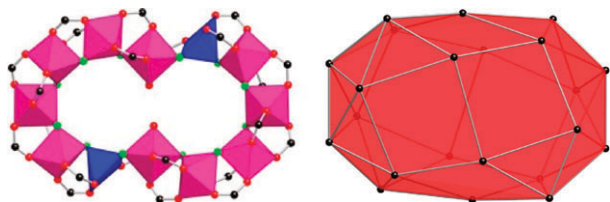
Fig. 130 An SBU with twenty-two points of extension:[229] Cr, pink; Cu, blue; C, black; O, red; Cl, green.
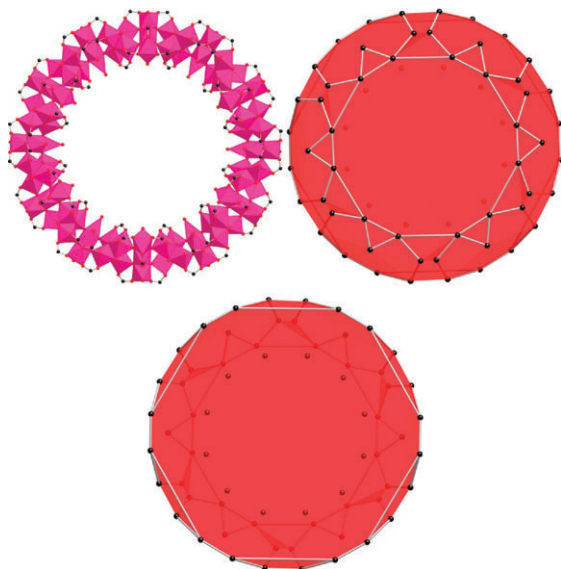
Fig. 131 An SBU with sixty-six points of extension:[238] Mn, pink; C, black; O, red.

Sixty-six points of extension

Eighty-four Mn atoms form a ring of edge sharing and corner sharing octahedra with 72 O atoms, and capped by 66 carboxylates, all bridging adjacent Mn atoms (Fig. 131).[238] Twelve carboxylates point into the ring, while the remaining carboxylates point out of or above the ring; no carboxylates point below the ring.

Concluding remarks

We exhibited the variety within the almost forgotten arsenal of discrete metal carboxylates could be employed in the design and construction of metal–organic frameworks. We expect that each one of these SBUs will endow the corresponding MOF with yet unpredictable stability and physical properties.

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