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Cobalt and Nickel Oxide Architectures in Metal Carboxylate Frameworks: From Coordination Polymers to 3D Inorganic Skeletons

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This microreview is devoted to the synthesis and properties of nickel and cobalt polycarboxylates, which are classified in terms of the geometries of the organic moieties. It is divided into three main sections — dicarboxylates, tricarboxylates and tetra- and hexacarboxylates — and discusses the extreme diversity of these architectures. Numerous topologies can be obtained, ranging from coordination polymers to 3D inorganic skeletons. This microreview begins with the widely studied cobalt succinate system, for which, to date, seven compounds have been reported. Then, examples from malonate to pimelate illustrate the influence of the length of the organic ligand, whereas examples from fumarate to diphenate illustrate the effects of rigidity and complexity. In the same way, examples from trimesate to mellitate show the effects of "multiconnecting" organic partners. These latter seem to disadvantage metal oxide condensation, since the two 3D inorganic frameworks contain linear dicarboxylate ions. On the other hand, 3D nickel oxide skeletons seem to be easier to synthesise than cobalt ones. Moreover, under similar hydrothermal conditions, using cobalt and nickel generally leads to different architectures.

Introduction

The wide utility of zeolites in the domains of catalysis, gas separation and ion-exchange has provoked widespread interest in new families of nanoporous materials.[1] Moreover, the opportunity to combine the exciting functionality of transition metal compounds, such as magnetic, electronic conductivity and optical properties, with the porosity of zeolites has become very attractive.[2] The first examples of 3D open frameworks incorporating transition metals were alumino- and gallophosphates substituted by metal ions in the skeleton; those based on cobalt were found to be some of the most promising catalysts.[3] Pure 3D metal phosphates were then synthesised and our first investigations with nickel showed that it could generate microporous materials with novel 3D M–O–M connectivities with face-, edge- and/or corner-sharing polyhedra that present interesting catalytic properties and good thermal stability.[4] The use of phosphate usually reduces electronic interactions and the preparation technique is, most of the time, a limiting factor for obtaining large pores. Indeed, metal phosphates are usually obtained by a templating method, therefore the removal of organic cationic templates generally leads to the collapse of the network. New synthetic approaches avoiding templating agents were therefore developed, with the use of donor ligands that can be part of the framework.[2] In this respect, the ability of carboxylates to strongly connect cobalt and nickel is very fruitful for building new architectures and often leads to a readily accessible porosity as well as physical properties that are usually encountered in dense solids.

The aim of this microreview is to focus on the structural variety and properties of nickel and cobalt polycarboxylates. The diversity of these organic partners offers a great potential to modulate structural architectures and the use of hydrothermal conditions considerably enlarges the range of possible arrangements arising from a metal and an organic molecule. Moreover, the electronic properties of cobalt and nickel significantly extend the potential applications of this type of compounds, especially in the field of porous magnetic materials. Although their ionic radii are similar, nickel and cobalt generally form different architectures. For Ni^{2+} (d^7) the ligand-field stabilisation energies strongly favour octahedral coordination, whereas for Co^{2+} (d^8) the tetrahedral environment is less disadvantaged.

The field of porous hybrid solids is very topical and is, of course, much wider. The use of oxalate, monocarboxylates or other organic linkers containing N-donor ligands (solely or in addition to carboxylates) will not be tackled here. For an overall overview of porous hybrid materials, we refer the reader to the reviews of Rao et al.,[5] which is devoted to metal carboxylates with open architectures, and of Kitagawa et al.,[6] which deals with functional porous coordination polymers.

The carboxylates presented in this review are classified in terms of the geometries of the organic partners. The first

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section is devoted to dicarboxylates and begins with the widely explored succinates. The influence of length, rigidity and complexity of the organic moieties is then presented. The second and the third parts are devoted to tricarboxylates and tetra- and hexacarboxylates, respectively.

Dicarboxylates

The Case of Succinate

The best characterised system of transition metal polycarboxylates is the cobalt succinate family. Altogether, seven phases containing cobalt, succinate, water and hydroxide have been discovered, mainly by varying the reaction temperature. The first of the series, $[Co(H_2O)_4(C_4H_4O_4)]$ (**1**), which is obtained at room temperature, was first identified in the Sixties[7] and is constructed from chains of cobalt octahedra bridged by succinate ions.[8] Upon increasing the temperature, inorganic condensation occurs to form edge-sharing octahedral trimers linked by carboxylates into the one-dimensional polymer $[Co(H_2O)_2(C_4H_4O_4)]$ (**2**).[9] A higher degree of condensation occurs under hydrothermal conditions, leading to the formation of open networks with extended M–O–M connectivity. $[Co_5(OH)_2(C_4H_4O_4)_4]$ (MIL-9, **3**), synthesised by Livage et al.,[10] is a nice example of a 2D metal oxide framework pillared by an organic moiety in a 3D coordination polymer. It is constructed from zig-zag layers of edge-sharing cobalt octahedra that generate 12-membered ring cavities with a lozenge shape (Figure 1, a). Half of the succinates are localised within the windows and the other half act as bridges between the sheets. In a more dilute medium, $[Co_4(OH)_2(H_2O)_2(C_4H_4O_4)_3{\cdot}2H_2O]$ (MIL-16, **4**) is formed.[11] It contains a 2D oxide network with 14-membered ring windows (Figure 1, b) and can easily be described as parallel "helicoidal" chains (light grey) connected by tetrameric units of co-planar octahedra (dark grey). Occluded and coordinated water can be removed from this compound in a reversible process. $[Co_6(OH)_2(C_4H_4O_4)_5{\cdot}H_2O]$ (**5**), synthesised by Long et al., is three-dimensional.[12] It presents layers similar to those of MIL-16 with the same helicoidal chains (light grey) but with the tetramers being replaced by dimers of edge-sharing square pyramids (dark grey, Figure 1, c). Four deprotonated succinates are located around the layers, although only one acts as a pillar. The originality of this compound lies in the presence of penta- and hexacoordinate metal centres, which are rather rare in the family of cobalt carboxylates. Forster et al. have recently demonstrated that these five compounds, and also **8**, which was previously obtained with nickel and is described below, can be obtained from the same starting mixture simply by varying the temperature.[9,13] The overall dimensionality of the materials, as well as the degree of M–O–M condensation, increases with temperature. The compounds present chains up to 125 °C, then the inorganic skeleton is two-dimensional, and above 190 °C a 3D overall dimensionality is observed (see Figure 2).[13]

Changing the solvent to a methanol/water mixture, at room temperature, leads to $[Co_3(OH)_2(H_2O)_4(C_4H_4O_4)_2{\cdot}6H_2O]$ (**6**).[14] This hybrid presents an interesting architec

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Carine Livage studied chemistry in the University of Orsay (Paris XI) and received her Ph.D. degree in 1991 working on the synthesis of molecular conductors and their characterisation under the supervision of Dr. Patrick Batail in the Laboratoire de physique des solides. (1991–1993). She undertook postdoctoral research in the group of Professor Lisa Klein in the Department of Ceramics of Rutgers University (New Jersey, USA) on the solution syntheses of ferroelectric thin films. She joined the Department of Chemistry of the University of Versailles in 1993 as an associate professor. Her field of research is mainly directed toward the synthesis and characterisation of porous transition metal hybrids.

Gérard Férey was born in Normandy, France, in 1941. After education in Caen, he became Professor at Le Mans University and moved to Versailles in 1996 to create the Institut Lavoisier. After a long period dedicated to magnetic inorganic fluorides, he is currently interested in the field of inorganic and hybrid porous solids in which he develops a global approach to these phases, from synthesis to applications through the mechanisms of reaction and prediction of structures. He is now Professor at the Institut Universitaire de France and member of the French Academy of Sciences.

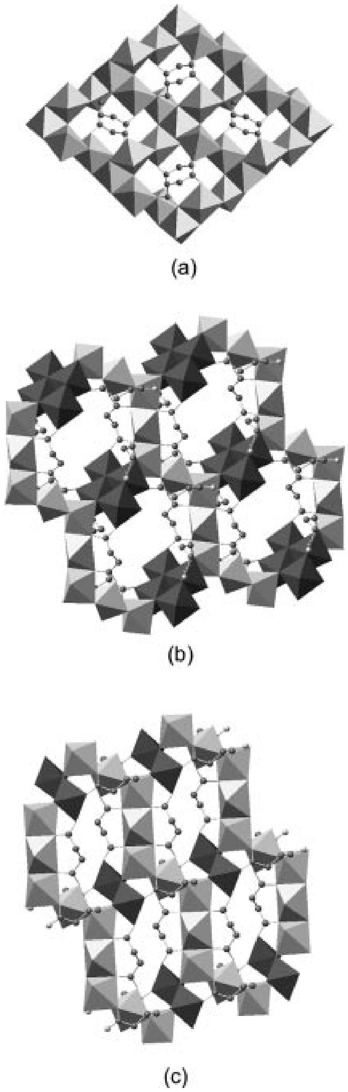


Figure 1. (a) Polyhedral representation of the 12-membered ring cavities lined by organic moieties in MIL-9 (**3**); (b) polyhedral view of MIL-16 (**4**) showing the connectivity between cobalt octahedra within the tetrameric unit (dark grey) and the helicoidal chain (light grey); (c) polyhedral view of **5** showing the connectivity between dimers of square pyramids (dark grey) and the helicoidal chain (light grey).

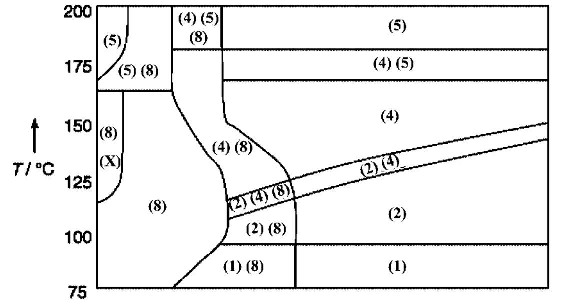


Figure 2. Crystallisation diagram in the succinate system (reproduced with permission from A. K. Cheetham[13]). The phases are indicated by their number code. The phase labelled X is still unknown.

ture that is often encountered with rigid linkers. Its structure can be described as metal oxide chains linked by the organic moiety into a 3D architecture with lozenge-shaped tunnels (see Figure 7). This topology bears a striking resemblance to a vanadium terephthalate isolated by Barthelet et al.[15]

As shown by these few examples, metal organic frameworks obtained with cobalt often exhibit interesting open architectures, although metal oxide condensation is most of the time "classical" with edge- or corner-sharing polyhedra. The architectures obtained hydrothermally with nickel, even though its radius and electronegativity are nearly identical to those of cobalt, are often different and the inorganic condensation more diverse. To date, two nickel succinate compounds have been described. Forster and Cheetham obtained the first metal carboxylate to present a three-dimensional oxide network, namely $[Ni_7(OH)_2(C_4H_4O_4)_6(H_2O)_2\cdot 2H_2O]$ (**7**).[16] Its structure can be described as layers of edge-sharing octahedra constructed from circular 12-rings surrounded by six truncated triangular 15-rings (Figure 3, a). The three-dimensionality is ensured by "isolated" corner-sharing octahedra (dark grey in the inset of Figure 3, a). This arrangement leads to a remarkable honeycomb framework with 1D pores lined by succinate anions. $[Ni_7(OH)_6(C_4H_4O_4)_4(H_2O)_3\cdot 7H_2O]$ (MIL-73, **8**), which is obtained under similar synthetic conditions, presents hybrid layers constructed from corrugated chains of nickel oxide connected by succinate ions (Figure 3, b).[17] The inorganic chains are made from hexanuclear metallic octahedral units (light grey) connected by a seventh octahedron (dark grey).

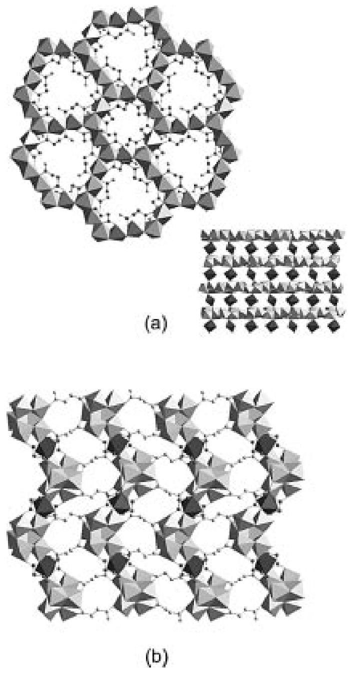


Figure 3. (a) View of a single nickel oxide layer in **7**; connection of the layers through isolated corner-sharing octahedra (dark grey) is shown in the inset; (b) view of one hybrid layer of **8**, where hexanickel units (light grey) are connected to bridging Ni octahedra (dark grey). Decorating succinate ions are represented in dark grey and bridging ones in light grey.

This hexameric unit is unusual and is built up from a dimer of face-sharing octahedra grafted onto a tetramer formed by two edge-sharing dimers connected by their corners. A pseudo-3D framework is formed due to the presence of strong hydrogen bonds between adjacent layers. This arrangement presents hydrated channels, where water molecules can be easily removed and reabsorbed. An isostructural phase has recently been obtained with cobalt using high-throughput synthesis.[18] Its structure, as determined by X-ray single crystal diffraction, confirmed the accuracy of the ab initio structural investigation of the nickel analogue, in spite of its high complexity due to the large number of independent atoms.

Changing the Length of the Aliphatic Chain

The reaction of malonic acid with transition metal ions has been reported, but most of the time in the presence of an additional co-ligand such as 2,2′-bipyrimidine.[19] One 2D cobalt malonate, **9**, which is isostructural with a nickel compound, has been obtained by Delgado et al.[20] Its structure consists of "isolated" metal octahedra connected through bridging carboxylate groups to four other metal centres (see Figure 4) to form layers with a pseudo square geometry.

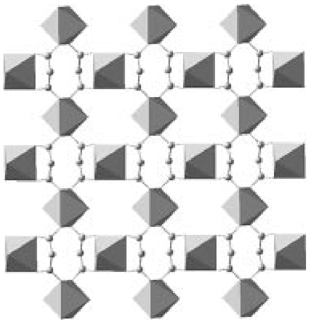


Figure 4. View of a layer of **9** showing the interconnection of metal octahedra through malonate ions.

Two compounds have been reported with glutaric acid: one with cobalt and the other with nickel. [$Co(C_5H_6O_4)$] (**10**), reported by Lee et al.,[21] is a 3D coordination polymer constructed from cobalt tetrahedra linked by glutarate anions. Its topology will be described below (Figure 6, b) with that of its pimelic acid analogue MIL-36.[26] Cubic [$Ni_{20}(H_2O)_8(C_5H_6O_4)_{20}\cdot 40H_2O$] (MIL-77, **11**), reported by us, presents an amazing chiral three-dimensional metal oxide network.[22] Its skeleton can be described as helices of edge-sharing octahedra connected to four parallel neighbouring ones through a nickel octahedron (dark grey in Figure 5, a). This induces the formation of perpendicular helices and generates corrugated 20-membered rings (Figure 5, b), which intersect to construct very large crossing tunnels in the [111] direction (Figure 5, c). The oxide framework is walled by two independent glutarate anions: the first one (light grey) is located on the twofold axis and the second one (dark grey) on the threefold one, with a statistical occupancy of 2/3. The nickel environments present bridging water molecules, and the tunnels contain disordered water molecules which can easily be removed by heating, leading to a porous compound (346 $m^2 g^{-1}$). MIL-77 is also a pure ferromagnet at low temperature. More recently, the adaptability of this 3D inorganic skeleton has been proved by obtaining the same topology with 3-methylglutaric acid.[23] The main difference between MIL-77 and this compound is the position of the second organic molecule. Unfortunately, this has drastic consequences for the porosity — its surface area is about half that of MIL-77.

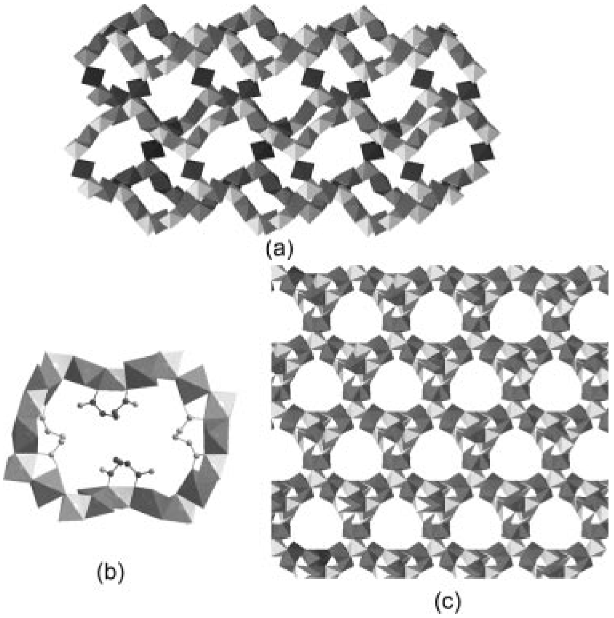


Figure 5. Views of the structure of MIL-77 (**11**): (a) view of six helices connected by nickel octahedra (dark grey); (b) polyhedral view of a corrugated 20- membered ring with the two independent glutarate ions; (c) view of the nickel oxide tunnels down [111].

Two compounds are obtained at room temperature upon increasing the aliphatic chain length by one carbon: [$Ni(H_2O)_4(C_6H_8O_4)$] (**12**),[24] which presents a 1D metal-organic chain and layered [$Co_2(H_2O)_6(C_6H_8O_4)_2\cdot 4H_2O$] (**13**).[25] The latter is constructed from corner-sharing octahedral chains where $Co(H_2O)_6$ shares its *trans*-H_2O molecules with two neighbouring [$CoO_4(H_2O)_2$] polyhedra (Figure 6, a). These chains are connected by adipates to generate the 2D open network.

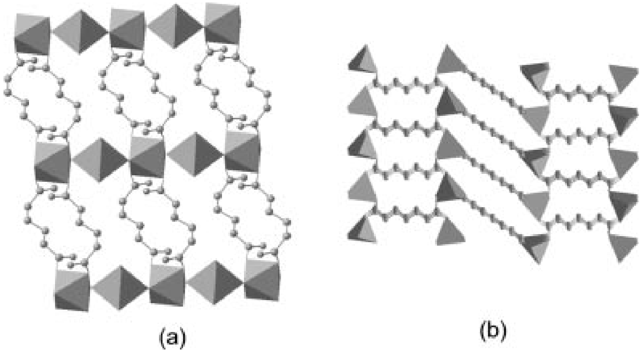


Figure 6. (a) View of a layer of **13** showing inorganic chains bound by adipate ions; (b) view of the 3D coordination polymer MIL-36 (**14**).

With pimelic acid, only [Co($C_7H_{10}O_4$)] (MIL-36, **14**) has been reported in the literature.[26] It is a 3D coordination polymer built up from cobalt tetrahedra where Co–CO_2–Co linkages give rise to infinite two-dimensional networks linked by the aliphatic chains. Therefore, hydrophobic carbon chains form the "walls" of two types of channels and act as spacers to generate an open structure (Figure 6, b). This type of arrangement has also been observed with adipate linkers.[27]

Using Unsaturated Chains

The use of fumaric acid leads to the formation of [$M_3(OH)_2(H_2O)_4(C_4H_2O_4)_2$·$2H_2O$] (**15**) with both cobalt and nickel, but with totally different synthetic procedures: the nickel compound was obtained under hydrothermal conditions[28] whereas its cobalt analogue was synthesised at 50 °C.[29] Their structure consists of chains of metal octahedra connected by fumarate ions to form a 3D framework (Figure 7). A remarkable feature is the presence of perpendicular intersecting tunnels. These have a large lozenge shape down the *a* axis and are delineated by four walls of fumarate-linked nickel oxide chains (Figure 7, a). The tunnels down the *b* axis are delimited by the space between two fumarate pillars (Figure 7, b). The repeating structural motif in the metal oxide chain is a trimer consisting of two edge-sharing octahedra linked by a μ_3-OH to a vertex of a third one (Figure 7, c). The carboxylic functions are bidentate and bridge successive metal atoms of the chains. It is interesting to note that the same topology can also be obtained with succinic acid.[14] The main difference concerns the aperture of the lozenge tunnels, which is more open in the case of the succinate. The cavity located at the intersection of the two perpendicular tunnels contains one water molecule for the fumarate and three for the succinate. Two other 1D compounds have been synthesised by Konar et al. simultaneously in the same batch: *cis*-[$Co(H_2O)_4(C_4H_2O_4)$·$2H_2O$] (**16**) and *trans*-[$Co(H_2O)_4(C_4H_2O_4)$] (**17**).[30] Both structures are built up from isolated cobalt octahedra linked by carboxylate in a bis-monodendate fashion. With acetylenedicarboxylic acid, only [$M(H_2O)_4(C_4O_4)$·$2H_2O$] (**18**) (M = Co, Ni) has been described.[31] Heating it to 100 °C leads to [$M(H_2O)_2(C_4O_4)$] (**19**). This latter solid presents a metal organic framework where octahedra are connected by dicarboxylate ligands into a compact 3D network.

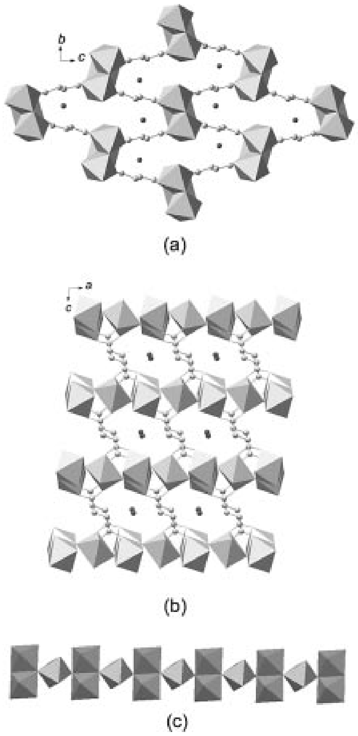


Figure 7. (a) View of the structure of **15** along *a* showing the lozenge-shaped tunnel topology; (b) view of the tunnels of **15** along the *b* axis; (c) the inorganic chain encountered in **6** and **15**.

Using Carboxylates Containing One Cycle

Two 3D compounds, namely [$Co_2(OH)_2$(1,4-BDC)] (**20**)[32,33] and [$Co(H_2O)_2$(1,4-BDC)] (**21**)[33] have been isolated with 1,4-benzenedicarboxylic acid (1,4-H_2BDC; also known as terephthalic acid). Compound **20** is built up from inorganic layers where two types of parallel tilted chains of edge-sharing octahedra are linked by OH bridges (Figure 8, a). The cobalt atoms of the light-grey chain are surrounded in the equatorial plane by four terephthalate oxygen atoms and in the apical positions by two OH groups, whereas those of the dark-grey chain are coordinated to four OH groups in the equatorial plane and two carboxylate oxygens. The layers are then connected together through terephthalate into a 3D architecture. The second coordination polymer, **21**, was obtained hydrothermally. Its structure

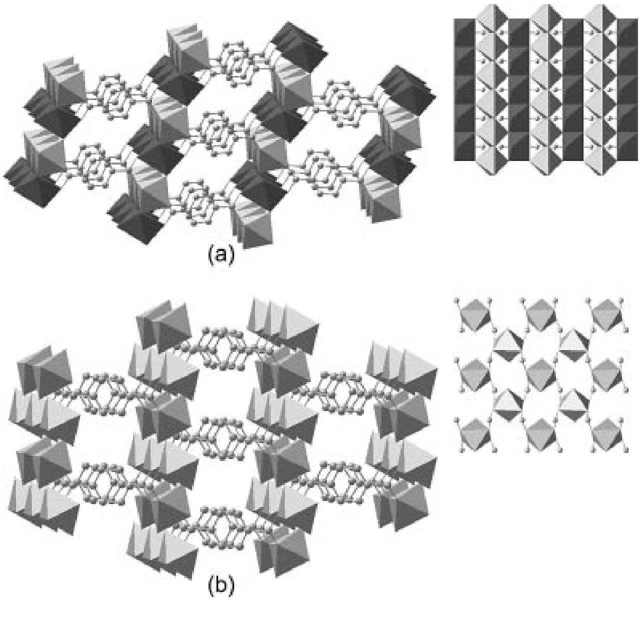


Figure 8. (a) Polyhedral view of the structure of **20** constructed from cobalt hydroxide layers (shown as inset) pillared by terephthalate ions; (b) polyhedral representation of the coordination polymer **21** with layers of a pseudo square symmetry shown as the inset.

presents isolated cobalt octahedra bridged by carboxylates into layers with a pseudo square symmetry (Figure 8, b). As for **20**, these layers are connected through terephthalate into a 3D network.

With 1,3-benzenedicarboxylic acid (1,3-H_2BDC; isophthalic acid) only one compound, namely $[Na_3\{Co_6O(OH)(1,3\text{-}BDC)_6\}\cdot H_2O]$ (MIL-104, **22**), has been reported.[34] Its structure is constructed from an unprecedented hexanuclear octahedral "cluster". The hexameric cobalt unit may be viewed as the association of two trimers connected through six μ_2-O vertices, each trimer being composed of octahedra sharing a central μ_3-O atom (Figure 9, a). The octahedra are highly distorted due to the chelating mode of one of the carboxylate groups. Indeed, the "bite" of the rigid acid group is too short for a cobalt octahedral coordination, therefore the angle is very narrow and Co–O distances are longer than usual. The architecture is a classical metal organic framework (MOF), with each hexamer joined by isophthalate ions to six neighbouring ones and serving as an octahedral node of a cuboid net (Figure 9, b). The small cavities left free by the hexamer packing are occupied by sodium cations. Each hexanuclear cluster is connected to six sodium ions to form a larger "super octahedron". In terms of "scale chemistry",[35] the topology is the same as that found for ReO_3, with $\{Na_6Co_6O_{26}\}$ units as giant octahedra.

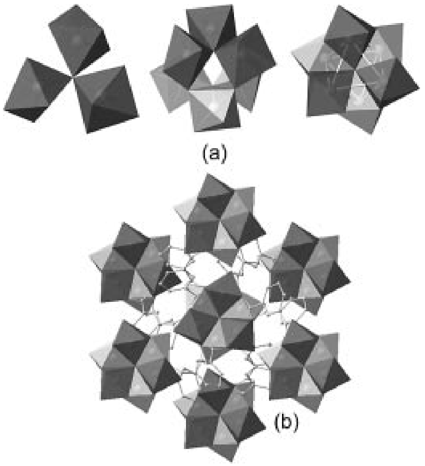


Figure 9. (a) Schematic representation of the hexameric unit of MIL-104 (**22**) showing its octahedral geometry; (b) projection of the structure showing the connection of one unit to six neighbouring ones that lie at the corners of an octahedron.

$[Co_3(OH)_2(C_8H_4O_4)_2]$ (**23**) has been obtained hydrothermally with phthalic acid.[36] Its 2D structure consists of inorganic layers of edge-sharing octahedra which generate eight-membered ring cavities (Figure 10). Phthalate ions are grafted onto the layers within the window and organic part is localised up and down the inorganic layer.

One cobalt compound $[Co(C_8H_8O_4)]$, (**24**) has been reported with 4-cyclohexene-1,2-dicarboxylic acid.[37] The originality of its structure lies in the tetrahedral coordination of the metal, which is less common than octahedral under hydrothermal conditions. It is interesting to note that the starting material was the *cis* form of the dicarboxylic acid whereas the resulting compound presents the *trans* one. Such changes are not unusual under hydrothermal conditions.[38] The structure is formed from isolated distorted tetrahedra linked by carboxylates into layers (see Figure 11). Two facing tetrahedra are first doubly bridged by carboxylates to form dimers, which are then bridged by the second carboxylate function to construct ribbons. These chains are connected through the organic moiety into a 2D network. As for the phthalate compound, the organic moiety is localised on the surface of the layer. As shown by these two last examples, the presence of a hydrophobic region opposite the carboxylate groups favours lamellar systems.

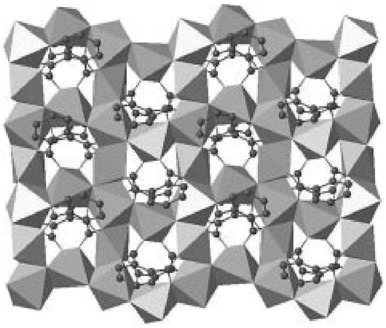


Figure 10. Polyhedral representation of **23** showing the eight-membered ring cavities lined by organic moieties.

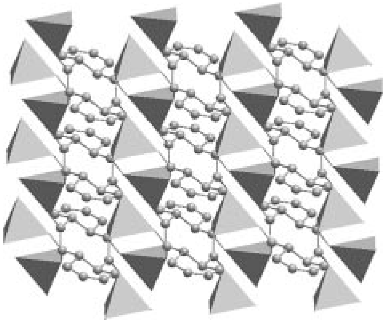


Figure 11. View of a layer of **24** showing the connection of cobalt tetrahedra by organic moieties.

The compound $[Co_5(OH)_8(CHDC)\cdot 4H_2O]$ (**25**) has been synthesised hydrothermally from 1,4-cyclohexanedicarboxylic acid (H_2CHDC).[39] Although the starting material was a mixture of *cis* and *trans* H_2CHDC, this compound is formed only with the *trans* conformation. Its structure is based on metal–hydroxide octahedral–tetrahedral layers pillared by dicarboxylate ions. These layers are closely related to the brucite type but with one out of every four octahedra removed and replaced by two tetrahedra above and below the layer (Figure 12). Each tetrahedron shares three corners with octahedra and the cobalt coordination is completed by unidentate carboxylate groups of CHDC pillars. A 3D framework is thus formed that contains channels filled with water. The dehydration–rehydration process is reversible, thereby conferring to this hybrid some porous properties. Removal of the water molecules leads to a shift of the layers combined with a tilt and a rotation of the organic moieties and a shortening of the interlayer space of about 1 Å (Figure 12). Moreover, this material presents a spontaneous ferrimagnetic magnetisation around 60 K, a temperature that is among the highest observed for this kind of compounds.

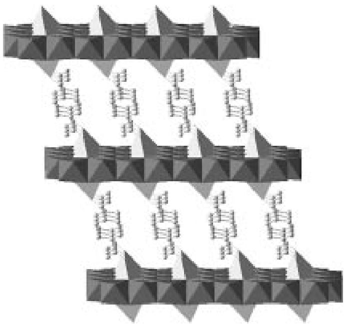


Figure 12. Polyhedral representation of $[Co_5(OH)_8(CHDC)]$, the anhydrous form of **25**; tetrahedra are represented in light grey and octahedra in dark grey.

Use of More Complex Aromatic Carboxylates

The coordination polymer $[Co(H_2O)_2(C_{10}H_6O_4)]$ (**26**) has been obtained hydrothermally with 4-carboxycinnamic acid.[40] Its structure presents the same topology as that described for its analogue obtained with terephthalic acid (**21**).[33] With 1,4-naphthalenedicarboxylic acid, one 3D hybrid compound, namely $[Co(C_{12}H_6O_4)]$ (**27**), has been obtained by Maji et al. (Figure 13, a).[41] Its structure is similar to that of the fumarates (**15**),[28,29] with chains of metal octahedra connected by an organic moiety into a 3D framework. The main difference between this structure and those previously described is the topology of the chain, which here is zig-zag and is only constructed from edge-sharing cobalt octahedra (Figure 13, c).

With 2,6-naphthalenedicarboxylic acid, only a 1D compound, namely $[M(H_2O)_4(C_{12}H_6O_4)]$ (**28**), has been reported with both cobalt and nickel. It is constructed from chains of isolated metal octahedra bridged by organic ions.[42]

Two compounds have been isolated under hydrothermal conditions using 1,1′-biphenyl-2,2′-dicarboxylic acid.[43] $[M(H_2O)_4(C_{14}H_8O_4)]$ (**29**) presents chains of isolated cobalt or nickel octahedra bridged by dicarboxylate ions. Nevertheless, a peculiar geometry of the organic moiety allows the formation of a chain with an interesting helical geometry (Figure 14, a). $[Co_6(OH)_2(H_2O)_4(C_{14}H_8O_4)_5]$ (**30**) is also 1D but with an infinite M–O–M connectivity. Its metal oxide chain is constituted of pentameric units of edge-sharing octahedra connected to its neighbour by a corner-sharing tetrahedron (Figure 14, b). The pentameric unit has a cross shape made of two linear trimers sharing a central octahedron.

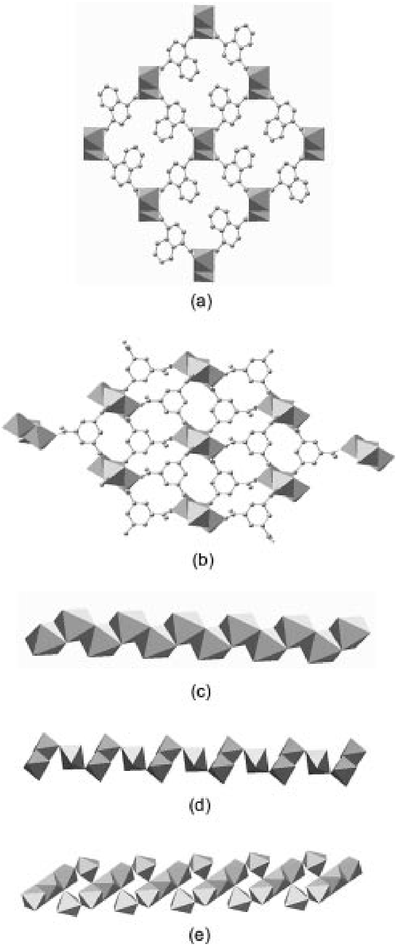


Figure 13. (a) View of the structure of **27** showing the lozenge-shaped tunnel topology; (b) view of the structure of **39** derived from the lozenge-shaped tunnel topology; (c) inorganic chain of **27** constructed from edge-sharing cobalt octahedra; (d) view of the chain of **39** with dimers of edge-sharing octahedra connected through a third octahedron by μ_2-OH_2; (e) view of the chain of **42** with linear trimers bridged through corner-sharing octahedra.

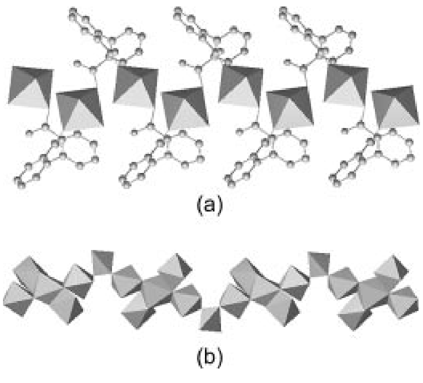


Figure 14. (a) View of a hybrid chain of **29** showing an interesting helical geometry; (b) representation of the oxide chain of **30** constructed from pentameric units of edge-sharing octahedra connected by a corner-sharing tetrahedron.

Tricarboxylates

Rigid, triangular 1,3,5-benzenetricarboxylic acid (H_3BTC), commonly named trimesic acid, has been extensively used to construct hybrid porous materials.[44] With cobalt and nickel, Yaghi et al. have reported the 1D polymer $[M_3(H_2O)_{12}(BTC)_2]$ (**31**) under hydrothermal conditions.[45] This compound, constructed from zig-zag chains of isolated octahedra connected through trimesate ions, can reversibly liberate eleven aqua ligands. The metal atoms at the centre of the sinusoid are surrounded by four water molecules in an equatorial plane, and the coordination environment is completed by two unidentate carboxylate ions (Figure 15, a). One side of the sinusoid is occupied by dangling carboxylate ions and the other one is taken up by metal octahedra. Compound **31** can also been obtained by thermal treatment of $[M_3(H_2O)_{14}(BTC)_2{\cdot}4H_2O]$,[46,47] the structure of which can be described as the juxtaposition of molecular motifs composed of three isolated octahedra linearly connected by two unidentate carboxylate ions. $[NaCo_3(OH)(H_2O)_{11}(BTC)_2{\cdot}1.5H_2O]$ (**32**) is another example of a 1D compound which has been synthesised at room temperature from trimesic acid.[47] Its structure consists of trinuclear units of *cis* edge-sharing metal octahedra, $\{Co_3O_6(\mu_3\text{-}OH)(\mu_2\text{-}OH_2)_2(H_2O)_5\}$, surrounded by three bridging carboxylate functions and connected by trimesate ions to construct the chains (Figure 15, b).

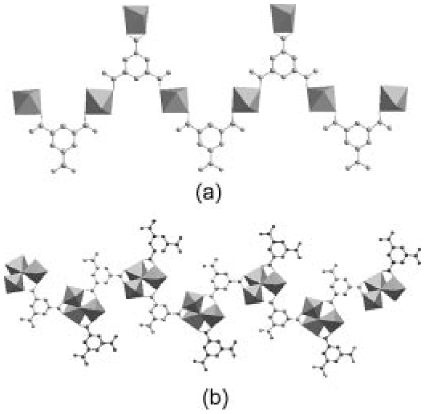


Figure 15. (a) View of a hybrid chain of **31** with isolated octahedra; (b) view of a hybrid chain of **32** showing trimers of edge-sharing octahedra.

$[Ni_3(H_2O)_8(BTC)_2]$ (**33**), a 2D compound obtained by us under hydrothermal conditions, is also constructed from $\{Ni_3O_8(\mu_2\text{-}OH_2)_2(H_2O)_6\}$ trimers.[48] These trimers are linear, with corner-sharing octahedra connected by μ_2-H_2O molecules, the stability of which is reinforced by the closeness of an unprotonated carboxylate and strong hydrogen bonds. Each trimer is surrounded by six carboxylate ions, two of which bridge the central nickel octahedron to its neighbour while the other four are unidentate (Figure 16, a). Six bridging trimesates connect each trimer to six neighbouring ones to construct an infinite 2D pseudo-hexagonal network. The planes are interpenetrated and positioned to favour π–π interactions (Figure 16, b). These planes can also be described as "double layers" of parallel organic rings connected through trimers.

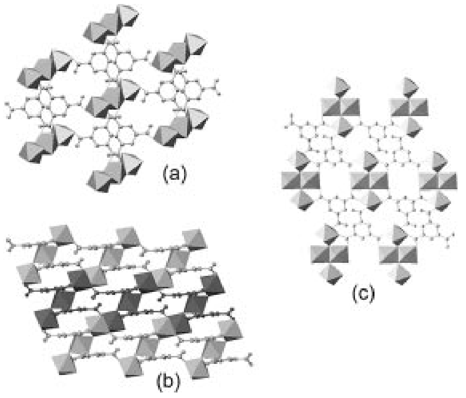


Figure 16. (a) Projection of the structure of **33** showing one nickel cluster connected to six equivalent ones; (b) view of the stacking of the layers of **33** dominated by π–π interactions; (c) view of the structure of **34** showing one nickel cluster connected to six equivalent ones.

$[Ni_2F(H_2O)_4(BTC){\cdot}2H_2O]$ (**34**) has been obtained by incorporating hydrofluoric acid into the starting hydrothermal mixture,[49] which is rather common for the synthesis of weakly soluble main group cations.[2] Its structure is very similar to that of **33** previously described and presents "double layers" of parallel organic rings, although here they are connected through tetrameric $\{Ni_4O_{10}(\mu_3\text{-}F)_2(H_2O)_8\}$ clusters, where the four nickel octahedra are connected by two μ_3-F atoms. Each tetramer is also connected to six neighbours through bridging trimesate ions (Figure 16, c). Four bridging carboxylates are in a planar arrangement in the tetramer, whereas the two additional monodentate ones are localised above and below this plane, which is here nearly parallel to the benzene rings.

$[Co_3(H_2O)_6(BTC)(HBTC)(H_2BTC){\cdot}2H_2O]$ (**35**) is also layered and its construction is dominated by π–π interactions with a mean interlayer distance of 3.4 Å.[50] The cobalt atoms have distorted octahedral environments, with carboxylate oxygen atoms in the four equatorial positions and water molecules in the apical ones. Distortion of the octahedra is due to the chelating connecting mode of one carboxylate. Due to this important distortion, only one carboxylate at a time can bind the metal in a chelating way and the metal environment is completed by monodentate ligands. The organic moiety acts as a triangular connector for the cobalt octahedra and presents the three states of protonation, which indicates that protonation depends not only on the pH of the medium but mostly upon condensation. This connection leads to the formation of a nearly planar infinite net with a pseudo-threefold symmetry that presents triangular cavities made from three cobalt octahedra and three trimesate ions (Figure 17, a), half of which are occupied by water molecules. The solid is formed by the stacking of six types of layers that are chemically identical but shifted (Figure 17, b). The only compound synthesised with trimesic acid that presents a 3D open structure is $[K\{Co_3(BTC)(HBTC)_2\}{\cdot}5H_2O]$, (**36**).[50] Its structure is based on sinusoidal chains of cobalt octahedra whose period is strongly correlated to the geometry of the organic molecule (Figure 17, c). The chains are connected to four other parallel sinusoids through two types of perpendicular carboxylates, leading to a 3D structure with rectangular tunnels. The oxide chains are constructed from dimeric units of edge-sharing octahedra that are connected by a vertex-sharing octahedron. The cobalt atoms of the dimer are surrounded by the organic moiety in a strongly distorted environment due to the chelating mode of one carboxylate. The protonated carboxylate group of HBTC points toward the centre of the channels delineated by four sinusoidal metal oxide chains connected by trimesate ions. Water molecules and potassium (in half occupancy) are located inside these rectangular tunnels (Figure 17, d).

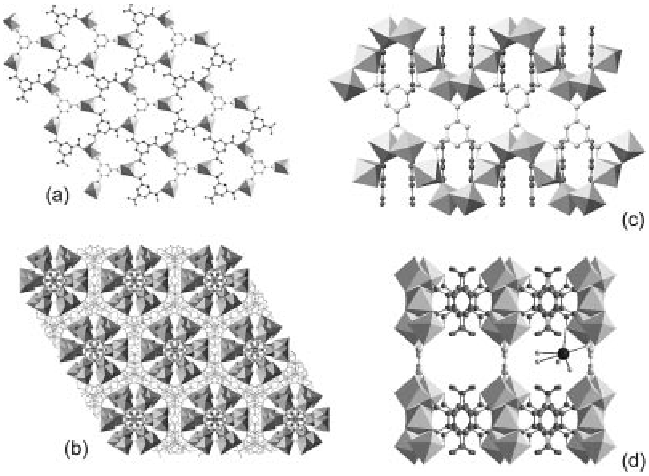


Figure 17. (a) Projection of one layer showing the triangular cavities in **35**; (b) projection of six equivalent layers in **35**; (c) projection of the structure of **36** showing the sinusoidal chains of cobalt octahedra; (d) view of two rectangular channels delineated by four cobalt and trimesate ions with a disordered potassium cation in **36**.

By changing the position of the carboxylate groups and using 1,2,3-benzenetricarboxylic acid (1,2,3-H_3BTC), two compounds have been obtained by Gutschke et al.[51] Both compounds, [$Co_2(OH)(H_2O)$(1,2,3-BTC)·H_2O] (**37**) and [$Co_2(OH)(H_2O)$(1,2,3-BTC)] (**38**), are constructed from inorganic chains presenting a Δ topology. In **37**, the chains are constructed from corner-sharing polyhedra, with a backbone where cobalt octahedra and tetrahedra alternate and on which pendant trigonal-bipyramids are grafted (Figure 18, a). These metal oxide strips run perpendicularly but never intersect. The connection of a chain to the orthogonal ones by carboxylate forms an amazing 3D network (Figure 18, b). In **38**, *trans* corner-sharing octahedra build the backbone of the chain, on which tetrahedra are attached by sharing edges with octahedra (Figure 18, c). Parallel chains are connected through the organic moiety to construct a 2D framework.

With *cis,cis*-cyclohexane-1,3,5-tricarboxylic acid (H_3CTC), one 3D hybrid compound with both cobalt and nickel, namely [$M_3(H_2O)_4(CTC)_2$·$5H_2O$] (**39**), has been synthesised hydrothermally by Kumagai et al.[52] It presents a structure derived from the lozenge-shaped tunnel topology with inorganic chains connected by the organic moiety. The four oxide chains in this compound are all connected through two central tricarboxylates (Figure 13, b) in one lozenge, and are slightly different to those reported previously. Dimers of edge-sharing octahedra are connected through a third octahedron which shares its *trans* vertices with two neighbouring dimers through a μ_2-OH_2 (Figure 13, d).

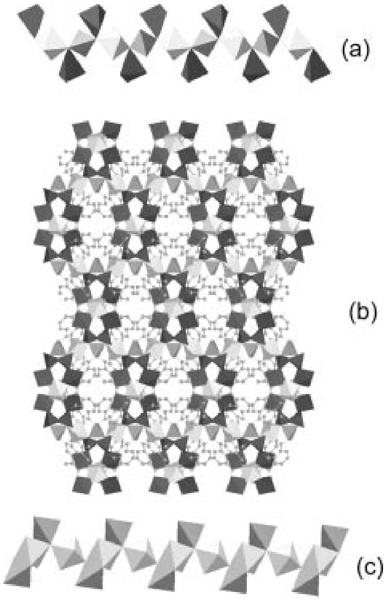


Figure 18. (a) View of the inorganic chain presenting a Δ topology in **37** with a backbone constructed from cobalt octahedra (light grey) and tetrahedra (medium grey), on which pendant trigonal bipyramids (dark grey) are grafted; (b) view of the structure of **37** showing the linking of the polyhedra by the organic moieties; (c) view of the inorganic chain presenting a Δ topology in **38** with a backbone constructed from cobalt octahedra (light grey), on which tetrahedra (medium grey) are grafted.

Tetra- and Hexacarboxylates

The three compounds synthesised hydrothermally with 1,2,4,5-benzenetetracarboxylic (pyromellitic) acid (H_4PM) have 3D architectures. [$Co_2(H_2O)_4(PM)$·$2H_2O$] (**40**) and [$Co_2(PM)$] (**41**) have been reported by Kumagai et al.[53] Compound **40** is a coordination polymer built up from cobalt octahedra bridged by carboxylates to construct layers with a pseudo square geometry similar to that observed in **20**. These layers are connected through organic moieties into a 3D network which presents cavities filled with water molecules. Compound **41** is formed from edge-sharing cobalt octahedra chains connected by pyromellitates.

[$Co_5(OH)_2(H_2O)_4(PM)_2$] (**42**) has been synthesised by Gutschke et al. simply by increasing the reaction temperature.[54] Its 3D structure is very similar to that of the fumarates (Figure 7) and presents, once again, lozenge-shaped tunnels with chains of cobalt octahedra connected by the organic moiety. Nevertheless, the topology of the oxide chain is really original, with parallel linear trimers of edge-sharing octahedra bridged by two corner-sharing octahedra (Figure 13, e).

With benzenehexacarboxylic (mellitic) acid (H_6MLT), only one 2D compound has been reported, namely $[Ni_4(OH)_2(H_2O)_6(MLT)]$ (**43**).[55] Its structure consists of inorganic chains generated by dimers of edge-sharing octahedra connected through a μ_3-OH group. These chains are further bridged by mellitates to construct corrugated layers.

Concluding Remarks

Although it is difficult to predict structures on the basis of the ligand and metal chosen, the results presented here allow us to draw some conclusions. This review reveals the extreme diversity of the cobalt and nickel oxide architectures obtained by the use of carboxylate ligands: "from coordination polymers to 3D inorganic skeletons". One of the reasons for the richness of these systems relates first to the electronic structure of Co^{2+} (d^7) and Ni^{2+} (d^8). Moreover, at variance with what is observed in templated metallophosphates[56] and metal organic frameworks based on Cu^{2+} and Zn^{2+},[57] in which the number of secondary building units (SBUs) is rather limited, the systems based on Co^{2+} and Ni^{2+} are, in terms of SBUs, extremely rich and diverse, and almost all structures present their own polyhedral building blocks. In the inorganic framework, one indeed observes monomeric moieties, in tetrahedral (Co) and octahedral (Ni, Co) coordination, along with dimers, trimers, tetramers, pentamers and hexamers with polyhedra sharing either vertices, edges or faces, as well as their connections into chains, layers and 3D networks (Figure 19). This diversity implies much more numerous possibilities of connection with the organic moieties, which are also numerous as shown in this review. Therefore, the exploration of the richness of these systems is still in its infancy, although careful attention must be paid to the experimental conditions as, besides the already shown effect of temperature and its influence on the condensation of the oligomers, the pH of the reaction mixture is also very important for the reactivity of these cations.

In terms of topologies, some of them are represented by one member, such as the remarkable honeycomb oxide framework with 1D pores of $[Ni_7(OH)_2(C_4H_4O_4)_6(H_2O)_2\cdot 2H_2O]$, whereas others appear regularly, with rigid or flexible organic molecules and with di- or tetracarboxylates. This is the case for the lozenge-shaped tunnel topology with inorganic chains connected by organic bridges. This architectural type is observed with both cobalt and nickel and has been obtained with dicarboxylates ions as diverse as small fumarate and cumbersome naphthalene-1,4-dicarboxylate and 1,2,4,5-benzenetetracarboxylate. These few examples demonstrate how much the oxide backbone can adopt diverse M–O–M connectivities to adapt to the organic moiety. More recently, this family has been enlarged with a new member obtained with 1,4-cyclohexanedicarboxylate, which presents the same chains as those observed with fumarate or succinate.[58,59] It is obvious that metal oxide condensation in solution is favoured by an increase of temperature. Nevertheless, it is interesting to note the counter-example of 1,4-cyclohexanedicarboxylate, which demonstrates the high complexity of these systems.[58] Indeed, simply by increasing the temperature from 140 to 170 °C, the lozenge-shaped tunnel topology is replaced by a layered compound constructed from remarkable hexanuclear prismatic nickel clusters (Figure 19l) connected through the organic moiety.

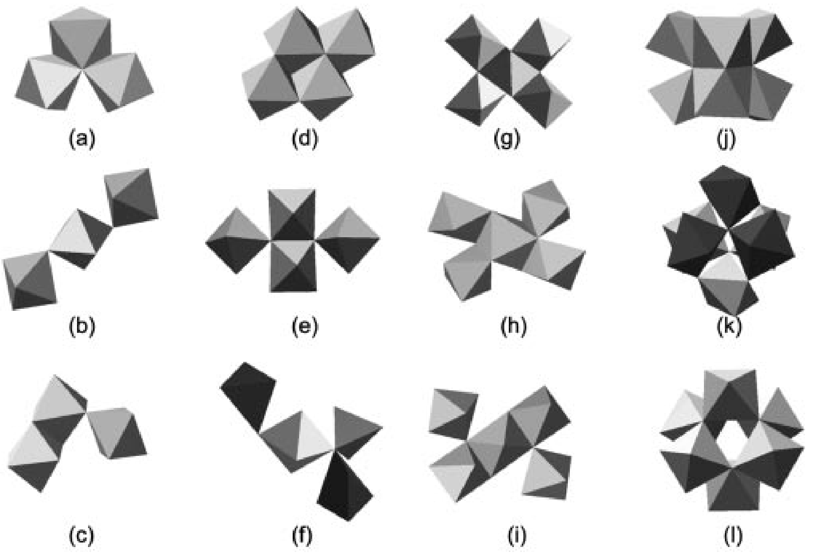


Figure 19. View of a few of the oligomers encountered in nickel and cobalt carboxylates: isolated trimers in **32** (a) or **33** (b) and the trimer of the inorganic chain of **39** (c); tetramers of the 2D oxide framework of MIL-16 (**4**, d), of the coordination polymer **34** (e), of the chain of **37** (f); pentamers of the inorganic layer of MIL-9 (**3**, g), of the oxide chains of **30** (h) and **42** (i); hexamers of the inorganic chains of MIL-73 (**8**, j) and those encountered in the coordination polymers MIL-104 (**22**, k) and $[Ni_6(OH)_6(C_8H_{10}O_4)_3(H_2O)_6\cdot 2H_2O]$ (l) reported recently.[58]

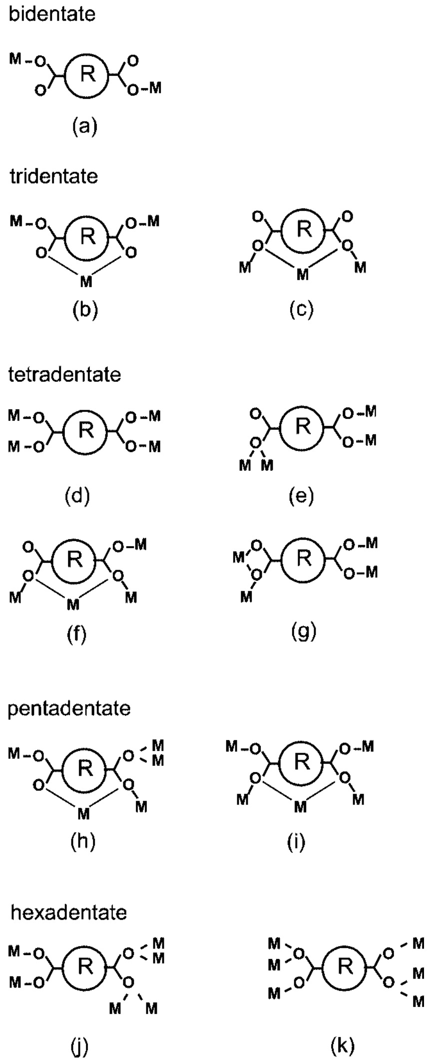
The topology of the extended inorganic network depends strongly on the geometry and connectivity of the organic partner. Inorganic condensation is favoured with small flexible organic molecules such as succinate but disfavoured with large and/or rigid ones. Glutarate is at the interface, since it allows the formation of an amazing 3D inorganic skeleton[22] as well as the construction of a metal organic framework with isolated tetrahedra.[21] With longer linear carboxylates, the final organisation is driven by weak interactions (hydrophobic) between alkyl chains.

In water, the use of rigid organic partners with benzene rings disfavours the formation of an extended oxide network and, most of the time, 3D coordination polymers or layered compounds dominated by π–π interactions are obtained. The example of the trimesate system illustrates the competition between covalent linkages and π–π interactions, which seems to be the decisive factor in the final architecture, well. It is difficult to draw rules from just two examples, but "multiconnecting" organics also seem to disadvantage oxide condensation. Indeed, the two 3D oxide frameworks have been synthesised with linear dicarboxylate ions. In both cases, the organic partner lines the oxide skeleton and is flexible enough to act as a chelate ligand for one metal via the oxygen atoms of neighbouring carboxylate groups. All modes of coordination of the organic moieties observed in the compounds described here are represented below. Only three coordination modes are present in the two 3D inorganic skeletons (modes c, i and f in Scheme 1). Mode a is mostly observed for 1D compounds with metal–organic chains, whereas mode d is present in several metal–organic frameworks (MOF). Others, such as modes b, e, g, h and j have been observed only once to date and seem to be rather scarce.

For tricarboxylates (see Scheme 2), the number of connecting modes is higher than the number of compounds and only one mode (j) has been observed in two compounds.

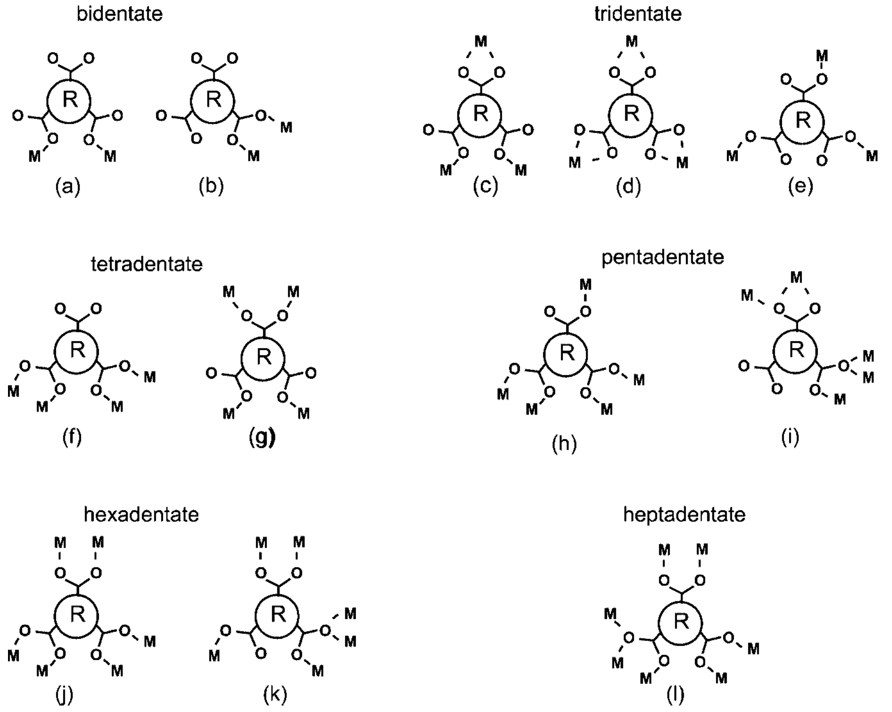
The connecting modes of tetra- and hexacarboxylates (Scheme 3) are also diverse and their number corresponds to that of described compounds. The ratio (number of metal atoms)/(number of organic moieties) (M/org) is given in Table 1 and varies from 1/2 for 1D compounds with metal–organic chains to 5 for **25**, which is constructed from hydroxide layers linked by organic pillars.[39] In the two 3D oxide frameworks, M/org is equal, or very close (7/6), to one.

Under hydrothermal conditions, the reactivity of cobalt and nickel is very different and similar synthetic conditions most of the time lead to totally different structural types. Isostructural compounds can sometimes be isolated but often under very distinct experimental procedures, as illustrated by the example of MIL-73, which is obtained hydrothermally with nickel and under reflux with cobalt. Under "basic" hydrothermal conditions it seems to be easier to isolate 3D inorganic skeletons with nickel than with cobalt. On the other hand, 2D oxide frameworks are very common with cobalt, whereas none have been isolated with nickel and polycarboxylates yet. Whereas only structures containing octahedra are reported for nickel carboxylates, the cobalt environment is more diverse, with the presence of tetrahedra and pentacoordinate metal. This is easily understandable in light of the coordinational flexibility of cobalt, which is higher than that of nickel due to its field anisotropy. On the other hand, the growth of nickel crystallites is most of the time limited compared to cobalt, therefore nickel compounds generally need structural determinations from powder diffraction data.

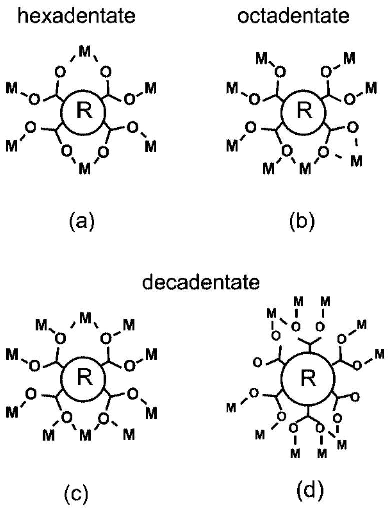


Scheme 1. Modes of coordination of the dicarboxylate ions observed in compounds **1**–**30**.

It is also interesting to comment here on the success of Neeraj et al. in the synthesis of sodalite networks based on cobalt and squarate,[60a] an organic moiety which is not so far from carboxylates. The six four-membered Al_2Si_2 rings of the sodalite cage are replaced here by the four-membered squarate (C4) rings, and are now linked by 12 cobalt octahedra instead of oxygen atoms. This organisation has already been encountered for a few other metal ions,[60b–60d] particularly nickel,[60b] and is therefore certainly a thermodynamically stable topology.



Scheme 2. Modes of coordination of the tricarboxylate ions observed in compounds **31**–**39**.



Scheme 3. Modes of coordination of the tetra- and hexacarboxylate ions observed in compounds **40**–**43**.

Magnetic measurements have been undertaken for most of the listed compounds and show diverse and usually extremely complicated behaviours, with competition between antiferromagnetic (AF) and ferromagnetic (F) interactions. This can be explained by the diversity of the inorganic networks and, of course, by their complexity. It is usual to have several independent metal centres, in a single architecture, showing various bond lengths and angles and sometimes, with cobalt, different geometries.

It is well known that connections with large M–O–M angles favour antiferromagnetic superexchange whereas connections with angles close to 90° favour ferromagnetic interactions,[61] although the M–O–C–O–M pathway should also be taken into account as well as the weak coupling between metal assemblies via organic bridges. The complexity of the M–O–M connectivity, as illustrated by MIL-73, in which octahedra are linked by faces, edges and corners, means that compounds often present interactions with different signs and strengths and are often frustrated. The only porous 3D oxide network described as a pure ferromagnet, MIL-77, is cubic with two independent octahedrally nickel atoms connected by sharing edges.

The two compounds with a lozenge-shaped topology and the same inorganic backbone, namely **15** and $[Ni_3(OH)_2(\textit{trans}\text{-}C_8H_{10}O_4)_2(H_2O)_4\cdot 4H_2O]$, both present a ferrimagnetic behaviour, with a lower critical temperature for the second compound, which may be due to the difference of the organic moieties.[59] $[Ni_3(OH)_2(\textit{cis}\text{-}C_8H_{10}O_4)_2(H_2O)_4\cdot 2H_2O]$ has also been synthesised recently by Kurmoo et al. and can be described as being formed from the same oxide chains but connected by a *cis*-1,4-cyclohexanedicarboxylate instead of a *trans* one.[59] It also exhibits a ferrimagnetic ordering that reversibly transforms into a ferromagnetic one upon partial dehydration, thus showing once again the complexity of the interaction pathways.

It is also not unusual that isostructural compounds obtained with cobalt and nickel display different dominant magnetic interactions[20,52] — antiferromagnetic for cobalt compounds and ferromagnetic for their nickel analogues.

Finally, the numerous nickel and cobalt carboxylates presented above illustrate the variety of structural architectures. Taking into account their great diversity, carboxylates

Table 1. Cobalt and nickel polycarboxylates.

Organic acid	Compound	M/org[a]	Dim.[b]	Synthesis	Mode[c]	Metal oxide connectivity	Magnetic interactions	Ref.
Succinic acid	$Co(H_2O)_4(C_4H_4O_4)$ (**1**)	1/1	0–1	room temp.	1–a	isolated octahedra	not given	[8]
	$Co(H_2O)_2(C_4H_4O_4)$ (**2**)	1/1	0–1	100 °C	1–cd	trimers of edge-sharing octahedra	not given	[9]
	$Co_5(OH)_2(C_4H_4O_4)_4$ (**3**) MIL-9	5/4	2–3	hydrothermal 180 °C	1–hj	edge-sharing octahedra	ferrimagnetic $T < 10$ K	[10]
	$Co_4(OH)_2(H_2O)_2(C_4H_4O_4)_3\cdot 2H_2O$ (**4**) MIL-16	4/3	2–2	hydrothermal 180 °C	1–ef	edge-sharing octahedra	ferrimagnetic $T < 10$ K	[11]
	$Co_6(OH)_2(C_4H_4O_4)_5\cdot H_2O$ (**5**)	6/5	2–3	hydrothermal 180 °C	1–di	CoO_5 and CoO_6 polyhedra	antiferromagnetic $T < 26$ K	[12]
	$Co_3(OH)_2(H_2O)_4(C_4H_4O_4)_2\cdot 6H_2O$ (**6**)	3/2	1–3	room temp.	1–d	edge-/corner-sharing octahedra	not given	[14]
	$Ni_7(OH)_2(C_4H_4O_4)_6(H_2O)_2\cdot 2H_2O$ (**7**)	7/6	3–3	hydrothermal 150 °C	1–fi	edge-/corner -sharing octahedra	paramagnetic	[16]
	$M_7(OH)_6(C_4H_4O_4)_4(H_2O)_3\cdot 7H_2O$ (**8**) M = Ni, Co MIL-73	7/4	1–2	hydrothermal 180 °C (Ni) under reflux (Co)	1–di	edge-/face-sharing octahedra	ferrimagnetic $T < 20$ K	[17]
Malonic acid	$M_2(H_2O)_4(C_3H_2O_4)_2$ (**9**) M = Ni, Co	1/1	0–2	60 °C	1–b	isolated octahedra	weak antiferromagnetic $T < 15$ K (Co), very weak ferromagnetic $T < 7.5$ K (Ni)	[20]
Glutaric acid	$Co(C_5H_6O_4)$ (**10**)	1/1	0–3	hydrothermal 180 °C	1–d	isolated tetrahedra	antiferromagnetic $T < 14$ K	[21]
	$Ni_{20}(H_2O)_8(C_5H_6O_4)_{20}\cdot 40H_2O$ (**11**) MIL-77	1/1	3–3	solvothermal 180 °C (water/ethanol)	1–ci	edge-sharing octahedra	pure ferromagnet $T_c \approx 4$ K	[22]
Adipic acid	$Ni(H_2O)_4(C_6H_8O_4)$ (**12**)	1/1	0–1	room temp.	1–a	isolated octahedra	paramagnetic	[24]
	$Co_2(H_2O)_6(C_6H_8O_4)_2\cdot 4H_2O$ (**13**)	1/1	1–2	room temp.	1–a	corner-sharing octahedra	not given	[25]
Pimelic acid	$Co(C_7H_{10}O_4)$ (**14**) MIL-36	1/1	0–3	hydrothermal 180 °C	1–d	isolated tetrahedra	antiferromagnetic $T < 20$ K	[26]
Fumaric acid	$M_3(OH)_2(H_2O)_4(C_4H_2O_4)_2\cdot 2H_2O$ (**15**) M = Ni, Co	3/2	1–3	hydrothermal 170 °C (Ni) 50 °C (Co)	1–d	edge-/corner-sharing octahedra	ferrimagnetic $T < 20$ K (Ni) paramagnetic (Co)	[28][29]
	cis-$Co(H_2O)_4(C_4H_2O_4)\cdot 2H_2O$ (**16**)	1/1	0–1	room temp.	1–a	isolated octahedra	not given	[30]
	trans-$Co(H_2O)_4(C_4H_2O_4)$ (**17**)	1/1	0–1	room temp.	1–a	isolated octahedra	paramagnetic	[29][30]
Acetylene-dicarboxylic acid	$M(H_2O)_4(C_4O_4)\cdot 2H_2O$ (**18**) M = Ni, Co	1/1	0–1	room temp.	1–a	isolated octahedra	not given	[31]
	$M(H_2O)_2(C_4O_4)$ (**19**) M = Ni, Co	1/1	0–3	by heating **18** at 100 °C	1–d	isolated octahedra	antiferromagnetic $T < 50$ K (Co and Ni)	[31]
Terephthalic acid	$Co_2(OH)_2(C_8H_4O_4)$ (**20**)	2/1	2–3	80 °C	1–k	edge-/corner-sharing octahedra	antiferromagnetic $T < 48$ K	[32][33]
	$Co(H_2O)_2(C_8H_4O_4)$ (**21**)	1/1	0–3	hydrothermal 120 °C	1–d	isolated octahedra	paramagnetic with AF coupling	[33]
Isophthalic acid	$Na_3Co_6O(OH)(C_8H_4O_4)_6\cdot H_2O$ (**22**) MIL-104	1/1	0–3	solvothermal 180 °C (water/ethanol)	1–g	hexamers of corner-sharing octahedra	antiferromagnetic $T < 50$ K	[34]
Phthalic acid	$Co_3(OH)_2(C_8H_4O_4)_2$ (**23**)	3/2	2–2	hydrothermal 200 °C	1–k	edge-sharing octahedra	not given	[36]
4-Cyclohexene-1,2-dicarboxylic acid	$Co(C_8H_8O_4)$ (**24**)	1/1	0–2	hydrothermal 180 °C	1–d	isolated tetrahedra	not given	[37]
1,4-Cyclohexane-dicarboxylic acid	$Co_5(OH)_8(C_8H_{10}O_4)\cdot 4H_2O$ (**25**)	5/1	2–3	hydrothermal 170 °C	1–a	edge-sharing octahedra and corner-sharing tetrahedra	ferrimagnetic $T < 60.5$ K	[39]
4-Carboxycinnamic acid	$Co(H_2O)_2(C_{10}H_6O_4)$ (**26**)	1/1	0–3	hydrothermal 120 °C	1–d	isolated octahedra	paramagnetic	[40]

Table 1. *(continued)*

Organic acid	Compound	M/org[a]	Dim.[b]	Synthesis	Mode[c]	Metal oxide connectivity	Magnetic interactions	Ref.
1,4-Naphthalenedicarboxylic acid	$Co(C_{12}H_6O_4)$ (**27**)	1/1	1–3	hydrothermal 170 °C	1–k	edge-sharing octahedra	intrachain: ferromagnetic interchain: antiferromagnetic T_c = 5.5 K	[41]
2,6-Naphthalenedicarboxylic acid	$M(H_2O)_4(C_{12}H_6O_4)$ (**28**) M = Ni, Co	1/1	0–1	room temp.	1–a	isolated octahedra	not given	[42]
Diphenic acid	$M(H_2O)_4(C_{14}H_8O_4)$ (**29**) M = Ni, Co	1/1	0–1	hydrothermal 170 °C	1–a	isolated octahedra	(Co) paramagnetic (Ni) paramagnetic with F (intrachain) and AF (interchain) couplings	[43a]
	$Co_6(OH)_2(H_2O)_4(C_{14}H_8O_4)_5$ (**30**)	6/5	1–1	hydrothermal 170 °C	1–dei	edge-sharing octahedra and corner-sharing tetrahedra	paramagnetic with AF coupling	[43b]
Trimesic acid (H_3BTC)	$M_3(H_2O)_{12}(BTC)_2$ (**31**) M = Ni, Co	3/2	0–1	hydrothermal 140 °C	2–ac	isolated octahedra	not given	[45]
	$NaCo3(OH)(H_2O)_{11}(BTC)_2\cdot 1.5H_2O$ (**32**)	3/2	0–1	room temp.	2–bf	trimers of edge-sharing octahedra	not given	[47]
	$Ni_3(H_2O)_8(BTC)_2$ (**33**)	3/2	0–2	solvothermal 180 °C	2–g	trimers of corner-sharing octahedra	paramagnetic with F coupling	[48]
	$Ni_2F(H_2O)_4(BTC)\cdot 2H_2O$ (**34**)	2/1	0–2	hydrothermal 150 °C	2–h	tetramers of edge and corner-sharing octahedra	not given	[49]
	$Co_3(H_2O)_6(BTC)(HBTC)(H_2BTC)\cdot 2H_2O$ (**35**)	1/1	0–2	hydrothermal 180 °C	2–de	isolated octahedra	paramagnetic with AF coupling	[50]
	$K[Co_3(BTC)(HBTC)_2]\cdot 5H_2O$ (**36**)	1/1	1–3	hydrothermal 180 °C	2–ij	edge-/corner-sharing octahedra	paramagnetic	[50]
1,2,3-Benzenetricarboxylic acid (1,2,3-H_3BTC)	$Co_2(OH)(H_2O)(1,2,3\text{-}BTC)\cdot H_2O$ (**37**)	2/1	1–3	hydrothermal 200-220 °C	2–j	corner-sharing octahedra, trigonal bipyramids, and tetrahedra	paramagnetic with AF coupling – spin frustration	[51]
	$Co_2(OH)(1,2,3\text{-}BTC)$ (**38**)	2/1	1–2	hydrothermal 200-220 °C	2–l	tetrahedra sharing edge with octahedra and corner-sharing octahedra	ferrimagnetic $T < 40$ K	[51]
cis,*cis*-Cyclohexane-1,3,5-tricarboxylic acid (H_3CTC)	$M_3(H_2O)_4(CTC)_2\cdot 5H_2O$ (**39**) M = Ni, Co	3/2	1–3	hydrothermal 170 °C	2–k	edge-/corner-sharing octahedra	(Co) dominant antiferromagnetic tending towards ferrimagnetic at low temp. (Ni) mostly ferromagnetic	[52]
1,2,4,5-Benzenetetra-carboxylic or pyromellitic acid (H_4PM)	$Co_2(H_2O)_4(PM)\cdot 2H_2O$ (**40**)	2/1	0–3	hydrothermal 110 °C	3–b	isolated octahedra	paramagnetic	[53]
	$Co_2(PM)$ (**41**)	2/1	1–3	hydrothermal 170 °C	3–a	edge-sharing octahedra	antiferromagnetic T_N = 16 K ferromagnetic $T < 13$ K	[53]
	$Co_5(OH)_2(H_2O)_4(PM)_2$ (**42**)	5/2	1–3	hydrothermal 190 °C	3–c	edge-/corner-sharing octahedra	not given	[54]
Benzenehexacarboxylic or mellitic acid (H_6MLT)	$Ni_4(OH)_2(H_2O)_6(MLT)$ (**43**)	4/1	1–2	hydrothermal 170 °C	3–d	edge-/corner-sharing octahedra	paramagnetic with AF coupling	[55]

[a] The "M/org" column refers to the ratio number of metal ions/number of organic moieties. [b] The first number in the "Dim." column refers to the M–O–M dimensionality and the second refers to the total dimensionality. [c] The "mode" column refers to the mode of coordination of the polycarboxylate ions (see Schemes 1–3).

are the partners of choice for constructing novel materials with interesting properties such as porosity, chirality or magnetism. Thus, much still remains to be understood in this field, although it is clear that very simple organic partners can lead to the most remarkable frameworks.

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