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Scandium-organic frameworks: progress and prospects

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Metal-organic frameworks (MOFs) represent a class of crystalline coordination compounds with periodic structures composed of metal cations or clusters connected by organic linkers. In recent years, increasing interest has been attracted to the synthesis and study of MOFs based on oxophilic cations of early transition metals, first of all, Zr^{IV}, Hf^{IV}, Ti^{IV} and Sc^{III}, and also main group Al^{III} cations. The carboxylate complexes of these metals possess high stability, which ensures the chemical robustness of the corresponding coordination polymers. The MOFs based on scandium(III) and oxygen-containing ligands are promising for the design of porous materials possessing high specific surface areas, high hydrolytic and thermal stabilities of the coordination framework and diverse functional properties. This review addresses the chemistry of metal-organic frameworks based on scandium(III). Published data on the synthesis and crystal structure characterization of scandium-containing coordination polymers available before 2018 are discussed. The properties of these compounds are considered.
The bibliography includes 101 references

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1. Introduction

The chemistry of metal-organic frameworks is among the most vigorously developing areas of modern science, which is evidenced by the explosive growth of the number of publications, reviews and books on this subject matter observed in the last decade.[1–9] Large specific surface area, regular crystal structure and extensive options for chemical functionalization make these compounds promising for gas storage,[10, 11] selective separation of molecules,[12–15] design of sensors[16, 17] and proton and ionic conductors[18–20] and so on. Many MOFs are suitable as heterogeneous catalysts,[21, 22] as they have accessible reactive sites such as coordinatively unsaturated metal cations in the channels and nanocavities.

Most of scientific publications related to MOFs address the synthesis of frameworks composed of polycarboxylate ligands and metals of the second half of the 3d transition series such as Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Cu^{II} and Zn^{II}. Despite the presence of interesting sorption, catalytic, luminescent,

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magnetic and other properties, these compounds do not possess sufficient chemical and/or thermal stability to be used in real industrial processes. Therefore, in recent years, increasing attention has been attracted by the synthesis and studies of MOFs based on oxophilic metals of the early parts of transition series, first of all, Zr^{IV}, Hf^{IV}, Ti^{IV} and Sc^{III} and chemically similar Al^{III}, the carboxylate complexes of which are highly stable, which ensures high stability of their coordination polymers. It is noteworthy that the chemistry of Zr^{IV}-based metal-organic frameworks has been comprehensively surveyed,[23, 24] unlike that of Sc^{III}-based MOFs.

Scandium has attracted special attention of researchers in relation to the development of microelectronics, rocket engineering and other advanced fields of technology. Scandium compounds are known to be used for manufacturing high-temperature ceramics, quantum amplifiers, lasers, luminophores, emission materials, dielectrics, solid electrolytes, high-power lighting halogen lamps, catalysts and so on.[25] Scandium doping of metal alloys endows the alloys with a variety of useful properties, in particular, high thermal stability, enhanced strength and corrosion and radiation resistance. The position of scandium in the Periodic Table is quite specific. Being the first d-element, it cannot be regarded as a typical d-element because of a relatively small cation radius and quite a few free orbitals. The coordination number (C.N.) of scandium(III) is usually six, but compounds with C.N.s from 3 to 9 are also known. According to Pearson's principle, the scandium(III) cation is a hard acid; therefore, it tends to form stable coordination compounds with O-donor ligands, in particular, oxo, hydroxy and carboxy complexes and complexes with N-oxide, sulfonate and carboxylate ligands of non-aromatic, aromatic and heterocyclic series. The scandium(III) cation does not possess redox properties and its compounds have low or moderate toxicity. Scandium(III) triflate is known for its Lewis acidity and is used as the catalyst of organic reactions.[26, 27] Furthermore, scandium is the lightest transition metal, which gives rise to higher specific sorption characteristics of scandium-based porous materials compared with those of MOFs based on heavier cations, with the crystal structure being the same. Thus, MOFs based on scandium and oxygen-containing ligands are promising for the development of porous materials with high specific surface area, high hydrolytic and thermal stability of the coordination framework and diverse functional properties.

Table 1. Scandium-organic frameworks classified according to the type of ligand.

Compound	Common designation	Formula	Ref.	Compound	Common designation	Formula	Ref.
1		$[Sc(HCOO)_3]$	32 – 34	**26**		$\{(Me_2NH_2)[Sc(fdc)_2(H_2O)_2]\cdot 1.5\,MeCN\}$	73
2		$(tma)_2[ScK(HCOO)_6]$	35	**27**		$(Me_2NH_2)_2[Sc(fdc)_2(HCOO)]$	73
3		$[Sc(OAc)_3]$	36	**28**		$[Sc_2(fdc)_3(H_2O)_2]$	73
4		$[Sc(ClCH_2COO)_3]$	37	**29**		$[Sc(inic)_2(OH)(H_2O)]$	74
5		$\{[Sc_2(Gly)_6](ClO_4)_6\}$	38	**30**		$\{[Sc_3(imdc)_4(H_2O)_4](NO_3)\cdot H_2O\}$	74
6		$\{(NH_4)[Sc(ox)_2]\cdot 2\,H_2O\}$	35	**31**		$\{[Sc(pydc)(Hpydc)(H_2O)]\cdot H_2O\}$	75
7		$\{K[Sc(ox)_2]\cdot 2\,H_2O\}$	39	**32**		$\{[Sc_2(pydc)_3(H_2O)_4]\cdot 5\,H_2O\}$	75
8		$[Sc_2(suc)_{2.5}(OH)]$	40, 41	**33**		$[Sc(pydc)(H_2O)(NO_3)]$	75
9		$[Sc_2(squ)_3]$	42	**34**		$\{[Sc(pmdc)(ox)_{0.5}(H_2O)_2]\cdot 3\,H_2O\}$	35
10		$[Sc(fba)_3]$	43	**35**		$\{[Sc(pmdc)(OH)(H_2O)]\cdot H_2O\}$	35
11		$[Sc_2(bdc)_3]$	44 – 51	**36**		$\{[Sc_2(pmdc)(OH)_3Cl]\cdot DMF\cdot 2\,H_2O\}$	35
12		$[Sc_2(NO_2\text{-}bdc)_3]$	45, 47, 49	**37**		$[ScLi(pmdc)_2(H_2O)]$	76
13		$[Sc_2(NH_2\text{-}bdc)_3]$	45, 47, 52	**38**		$[ScNa(pmdc)_2(H_2O)]$	76
14	MIL-88 (Sc)	$\{[Sc_3O(bdc)_3(H_2O)_3]\cdot 0.5\,Cl\cdot$	53, 54	**39**	PCN-332 (Sc)	$[Sc_3O(bttc)_2(H_2O)_3(OH)]$	77
		$\cdot 0.5\,(OH)\cdot 4\,(DMF)\cdot 3\,(H_2O)\}$		**40**	PCN-333 (Sc)	$[Sc_3O(tatb)_2(H_2O)_3(OH)]$	77, 78
15		$\{[Sc_3O((HO)_2\text{-}bdc)_3(H_2O)_3](NO_3)]\}$	55	**41**	RPF-12	$[Sc_2(1,5\text{-}nds)(OH)_4]$	79
16		$\{[Sc_3O(bpdc)_3(H_2O)_3](OH)\}$	56	**42**	RPF-13	$[Sc_2(2,6\text{-}nds)(OH)_4]$	79
17	MIL-68 (Sc)	$[Sc(OH)(bdc)]$	56	**43**		$[Sc_3(dsb)_2(O_2H_3)(OH)_2(H_2O)_2]$	80
18	MIL-53 (Sc)	$[Sc(OH)(bdc)]$	54, 57 – 59	**44**		$[Sc_3(dsb)_2(OH)_3(H_2O)_4]$	80
19		$[Sc(OH)(NO_2\text{-}bdc)]$	45	**45**		$[Sc_3(dsb)(OH)_6(H_2O)]$	80
20	MIL-101 (Sc)	$[Sc_3O(bdc)_3(H_2O)_3(OH)]$	56, 60	**46**		$[Sc(dsb)(phen)(H_2O)](H_2O)$	80
21	MIL-100 (Sc)	$[Sc_3O(btc)_2(H_2O)_3(OH)]$	54, 56, 61 – 65	**47**		$[Sc(bpyO)_3(NO_3)_3]$	81
22		$[Sc_3O(btb)_2(H_2O)_3(OH)]$	53	**48**		$\{[Sc(bpyO)_3](CF_3SO_3)_3(MeOH)_{2.7}(H_2O)_3\}$	81
23	NOTT-400 (Sc)	$\{[Sc_2(bptc)(OH)_2]\cdot 1.25\,(H_2O)\}$	66 – 70	**49**		$\{[Sc(bpyO)_3](ClO_4)_3\}$	81
24	*soc*MOF (Sc)	$[Sc_3O(abtc)_{1.5}(H_2O)_3(NO_3)]$	54, 56, 71	**50**		$\{[Sc(bpyO)_4(H_2O)_2](ClO_4)_3\}$	81
25	NOTT-401 (Sc)	$\{[Sc(tdc)(OH)]\cdot 2.6\,(H_2O)\}$	66, 68, 72				

Note. The following abbreviations for ligands are used: $abtc^{4-}$ is 3,3′5,5′-azobenzenetetracarboxylate, bdc^{2-} is terephthalate, $bpdc^{2-}$ is diphenyl-4,4′-dicarboxylate, $bptc^{4-}$ is diphenyl-3,3′,5,5′-tetracarboxylate, bpyO is 4,4′-bipyridine *N*,*N*′-dioxide, dsb^{3-} is 3,5-disulfobenzoate, btb^{3-} is 4,4′,4″-benzene-1,3,5-tiyltris(benzoate), btc^{3-} is trimesate, $bttc^{3-}$ is benzene-tris(thiophene)tricarboxylate, fba^- is 2,3,5,6-tetrafluoobenzoate, fdc^{2-} is furan-2,5-dicarboxylate, $imdc^{2-}$ is imidazoledicarboxylate, $inic^-$ is isonicotinate, ipa^{2-} is isophthalate, 1,5-nds^{2-} is 1,5-naphthalenedisulfonate, 2,6-nds^{2-} is naphthalene-2,6-disulfate, NH_2-bdc^{2-} is 2-aminoterephthalate, NO_2-bdc^{2-} is 2-nitroterephthalate, $(OH)_2$-bdc^{2-} is dihydroxyterephthalate, ox^{2-} is oxalate, phen is phenanthroline, $pmdc^{2-}$ is pyrimidine-4,6-dicarboxylate, $pydc^{2-}$ is pyridine-2,3-dicarboxylate, squ^{2-} is squarate, suc^{2-} is succinate, $tatb^{3-}$ is 4,4′,4″-triazine-2,4,6-triyltris(benzoate), tdc^{2-} is 2,5-thiophenedicarboxylate.

Despite the obvious benefits and prospects, the chemistry of scandium complexes and, in particular, scandium-organic frameworks (SOFs) is poorly developed. A considerable restraining factor is that scandium is a trace element and, correspondingly, scandium compounds are relatively expensive. In 1999, early reviews of the scandium(III) chemistry were published;[28,29] however, they did not provide a comprehensive picture of the research related to metal-organic frameworks. The subsequent publications either describe some scandium-based frameworks as examples of rare-earth coordination polymers [30] or address a part of such frameworks obtained by a particular research team.[31]

The present literature review is devoted to the chemistry of metal-organic frameworks based on scandium(III), including methods of synthesis, structural features and properties of SOFs, and covers publications up to the beginning of 2018. The review is structured according to the nature of the organic bridging ligand incorporated in the framework and consists of relevant subsections. For reader's convenience, the compounds mentioned in the review are numbered and listed in Table 1.[32–81]

2. Structure and properties of scandium-organic frameworks based on carboxylate ligands

2.1. Scandium-organic frameworks with non-aromatic ligands

The structural chemistry of SOFs based on non-aromatic carboxylate ligands (Fig. 1) is diverse, with chain-like, layered and framework architectures being present; cases of polymorphism are also encountered, that is, one and the same structural motif can give rise to different structures of the coordination frameworks. A specific feature of scandium(III) carboxylate coordination polymers is their structural similarity with the metal-organic frameworks called MIL (Materials of Institut Lavoisier) composed of other three-charged cations (Cr^{III}, V^{III}, Fe^{III}), which leads to some similarity of their coordination chemistry.[82]

A typical example of SOFs is scandium formate $[Sc(HCOO)_3]$ (**1**), which is the first Sc^{III}-containing coordination polymer to be studied by X-ray diffraction.[32,33] In the crystal structure of this compound, scandium cations (C.N. = 6) are surrounded by oxygen atoms of the bridging carboxyl groups, thus forming octahedra, which are connected by the bridging formate anions to form separate layers parallel to the (100) plane. These layers are connected to one another by other formate ligands. The formate ligands between the layers have the *syn–anti* configuration, whereas the bond configuration within the layer is *anti–anti*. Later, the structure of the orthorhombic polymorph of scandium formate was determined.[34] In the orthorhombic polymorph of compound **1**, the $\{ScO_6\}$ octahedra are connected into infinite chains that resemble the chains present in scandium acetate (see below).[36]

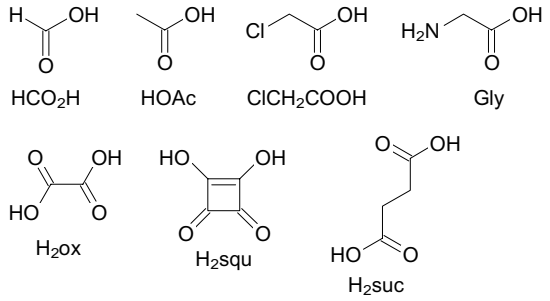


Figure 1. Types of non-aromatic carboxylate ligands.

An anionic scandium formate of a complex structure, $(tma)_2[ScK(HCOO)_6]$ (**2**; tma is tetramethylammonium), was prepared by the reaction of scandium chloride, 4,6-pyrimidinedicarboxylic acid, oxalic acid and potassium chloride in a DMF–methanol mixture under solvothermal conditions.[35] Formate anions and tetramethylammonium cations were formed *in situ* in this reaction. The authors do not detail the mechanism of formation of tetramethylammonium cations, which are generated during the synthesis instead of the expected dimethylammonium cations, which are often formed upon DMF hydrolysis. The formate anions connect the $\{ScO_6\}$ and $\{KO_6\}$ octahedra into a three-dimensional framework of primitive cubic topology (**pcu**)[83] and the cavities are occupied by ammonium cations (Fig. 2). It is of interest that the final compound contains neither pyrimidine-4,6-dicarboxylic acid nor oxalic acid (or their anions). The authors do not specify the role of these acids in the coordination polymer synthesis.

Similarly to the formic acid, acetic acid is also involved in various chain-like MOFs based on Sc^{III}. The structure of anhydrous scandium acetate $[Sc(OAc)_3]$ (**3**) was first described in 1984.[36] This compound can be obtained by the reaction of scandium oxide with acetic anhydride or by the reaction of scandium carbonate with acetic acid. According to X-ray diffraction data, this is a chain-like structure in which every Sc^{III} cation is located at the centre of an octahedron formed by six oxygen atoms of the carboxylate ligands, which in turn connect two neighbouring octahedra by triple bridges (Fig. 3). This architecture is

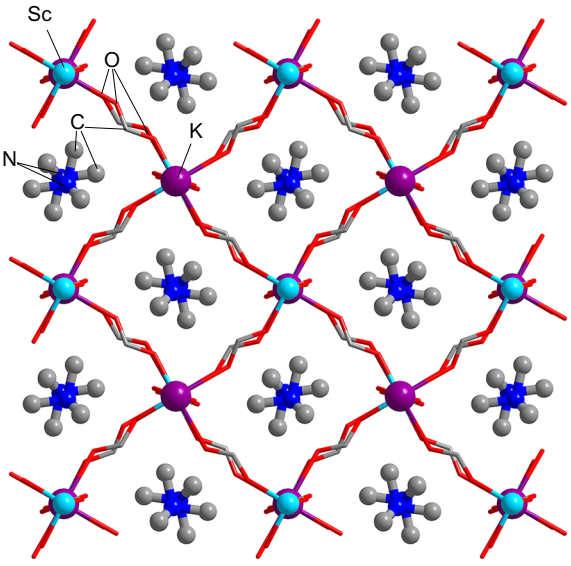


Figure 2. View of the structure of $(tma)_2[ScK(HCOO)_6]$ (**2**) along the *c* axis.[35]
The hydrogen atoms are omitted. The nitrogen and carbon atoms are disordered over two positions of tetramethylammonium cations and are shown as spheres.

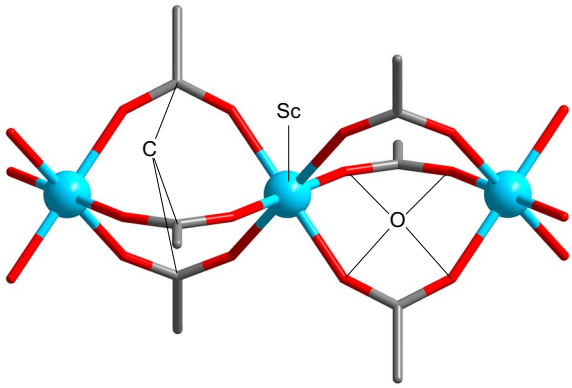


Figure 3. Structure of a chain of $[Sc(OAc)_3]$ (**3**).[36]
Here and in other Figures, the hydrogen atoms are omitted.

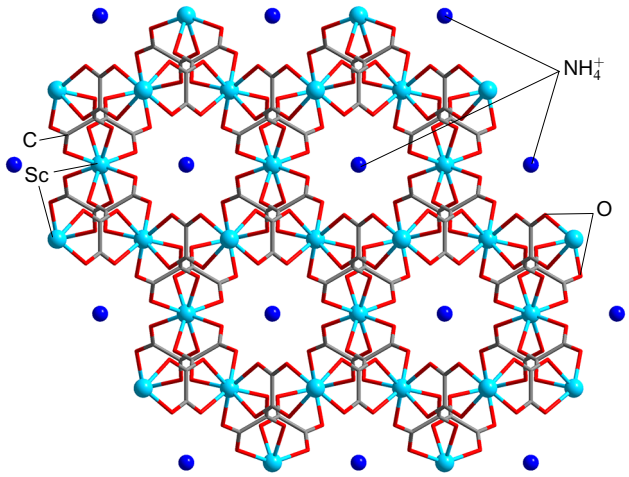


Figure 4. View of the structure of $(NH_4)[Sc(ox)_2]\cdot 2H_2O$ (**6**) along the *c* axis.[35]

common to a large number of scandium(III) carboxylates including the above-described scandium formate.

A similar structure is inherent in the frameworks based on chloro- and aminoacetic (glycine) acids, $[Sc(ClCH_2COO)_3]$ (**4**) (Ref. 37) and $\{[Sc_2(Gly)_6](ClO_4)_6\}$ (**5**),[38] which were prepared by slow evaporation of aqueous solutions of scandium hydroxide and chloroacetic acid or scandium perchlorate and glycine, respectively, at room temperature. The polymer chains of these compounds are connected to one another by intermolecular hydrogen bonds.

The structural chemistry of scandium oxalate-based MOFs is equally diverse. Owing to the chelation effect, the interaction between scandium(III) cations and oxalate anions is stronger than that in the case of ligands described above, which brings the metal C.N. to eight as a result of coordination of four oxalate ligands. The coordination polyhedron of scandium is a square antiprism in this case.

Scandium oxalate $(NH_4)[Sc(ox)_2]\cdot 2H_2O$ (**6**) was obtained by the reaction of scandium(III) chloride with 4,6-pyrimidinedicarboxylic acid and oxalic acid in water.[35] The Sc^{III} cations located at the centre of square antiprisms are connected by bridging oxalate anions, each anion connecting two cations. If each Sc^{III} cation in the coordination structure is considered as a lattice point, this gives a three-dimensional framework with a quartz topology (**qtz**) and a system of 3D channels. Cylindrical channels with a diameter of 3.6 Å run along a six-fold axis, the ammonium cations being rigidly held in the channels by hydrogen bonds (Fig. 4).

Slow evaporation of a solution of potassium nitrate, oxalic acid and scandium nitrate acidified by nitric acid at room temperature yielded colourless crystals with the composition $K[Sc(ox)_2]\cdot 2H_2O$ (**7**).[39] This compound is isostructural to compound **6**. The large K^+ cations occupy positions at the centres of hexagonal channels and are surrounded by four oxygen atoms of the oxalate carboxyl groups and by four oxygen atoms of water molecules. The researchers studied in detail the stages of thermal decomposition of this compound and emphasized that dehydration is reversible and that the behaviour of the guest water molecules is similar to that in zeolites.

When scandium nitrate and succinic acid (H_2suc) were allowed to react under hydrothermal conditions in the presence of triethylamine (pH 6), crystals of the coordination polymer $[Sc_2(suc)_{2.5}(OH)]$ (**8**) were isolated.[40] According to X-ray diffraction data, scandium atoms occur as the $\{Sc_2(OH)(COO)_2\}$ binuclear units (Fig. 5), in which the Sc^{III} cations are connected by two bridging carboxyl groups and one bridging hydroxide anion. These binuclear units are linked by bridging succinate ligands to form pseudolayers in the *ab* plane. In turn, the pseudolayers are connected in both directions along the *c* axis thus forming a framework. The authors specially emphasize high thermal stability (up to 500 °C) of the coordination polymer.

The subsequent studies addressed the catalytic properties of this compound. In particular, it was shown that polymer **8** catalyzes the Friedel–Crafts acylation of anisole.[40] However, the yield of the major product (*p*-methoxyacetophenone) does not exceed 30% after 24 h (Table 2, No. 1).

A considerably higher efficiency of $[Sc_2(suc)_{2.5}(OH)]$ was noted in the acetalization of carbonyl compounds[40,41] and oxidation of sulfides;[41] this illustrates the activity of compound **8** in the (Lewis) acid-base and redox reactions, respectively. Both reactions proceed under mild conditions and give products in high yields (see Table 2, Nos 2, 4, 5 and 7, 8, respectively). In the sulfide oxidation, an important factor is the amount of the oxidant used: in the presence of 1.1 equiv. of hydrogen peroxide, sulfoxide is formed as the major product (see Table 2, No. 7), whereas an excess of H_2O_2 induces further oxidation to give sulfone (see Table 2, No. 8).

Perles *et al.*[40,41] noted that compound **8** is stable in water and organic solvents and behaves as a heterogeneous catalyst in the above-described catalytic reactions, which markedly facilitates its separation from the reaction mixture. Furthermore, this catalyst can be used in at least four catalytic cycles without loss of activity.

Scandium squarate $[Sc_2(squ)_3]$ (**9**) was prepared under hydrothermal conditions by the reaction of scandium chloride and the squaric acid ($C_4O_4H_2$, H_2squ).[42] According to X-ray diffraction data, scandium cations are located in the octahedral environment formed by six oxygen atoms of the squaric acid anions (Fig. 6). It is worth noting that the structure contains zeolite-like cavities with a diameter of 6.8 Å, but the solvent-accessible volume is only 5%, which

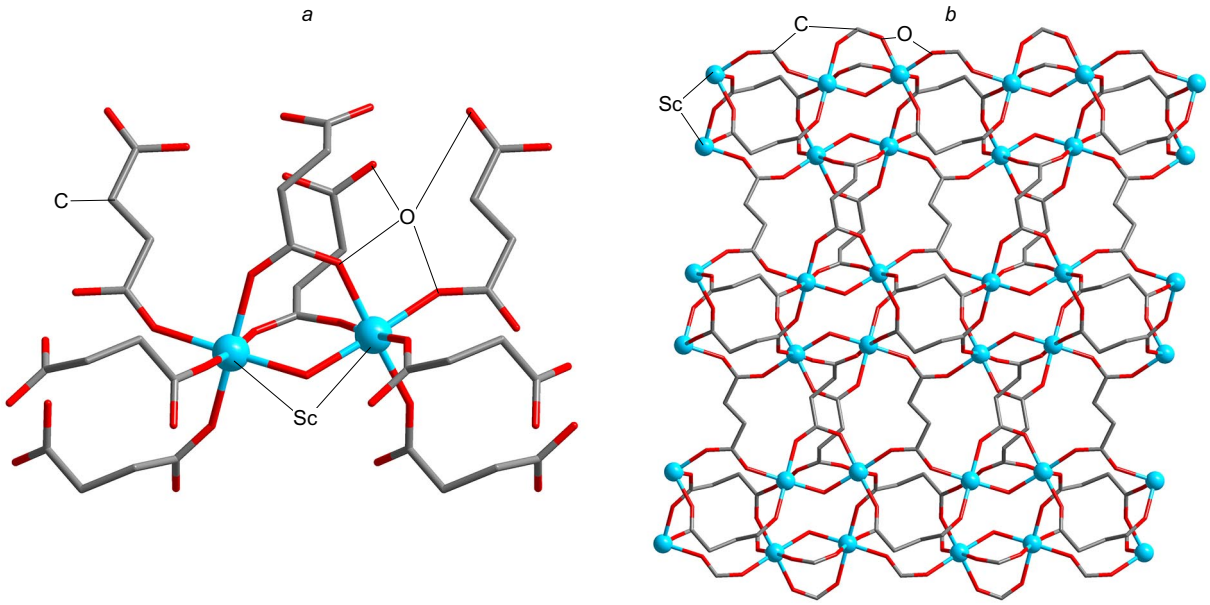
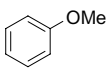
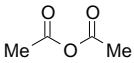
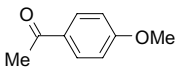
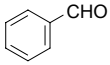
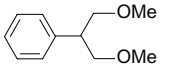
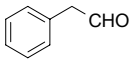
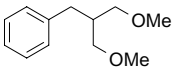
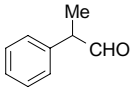
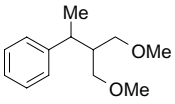
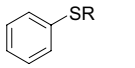
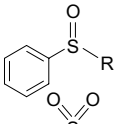
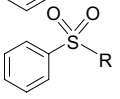
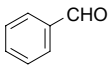
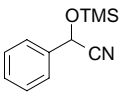
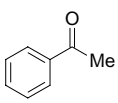
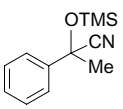


Figure 5. Binuclear building block (*a*) and view along the *b* axis (*b*) of the structure of $[Sc_2(suc)_{2.5}(OH)]$ (**8**).[40]

Table 2. Catalytic properties of $[Sc_2(sus)_{2.5}(OH)]$ (**8**) and $[Sc_2(squ)_3]$ (**9**) in acetalization and silylation of carbonyl compounds, Friedel – Crafts acylation and oxidation of sulfides.

No.	Substrate	Reagent	Reaction conditions			Product	Yield (conversion, %)	Ref.
			catalyst (mol.%)	*T*/°C	*t*/h			
1			**8** (< 5)	not indicated	24		30	40
2		$CH(OMe)_3$	**8** (8)	60 – 70	4		(70)	40, 41
3		$CH(OMe)_3$	**9** (5)	60	1		(100)	42
4		$CH(OMe)_3$	**8** (10)	60 – 70	4 days		70	41
5		$CH(OMe)_3$	**8** (5)	60	12		(65)	42
6		$CH(OMe)_3$	**9** (5)	60	12		(78)	42
7	 R = Me, CH_2CHEt_2	H_2O_2 (30%) (1.1 equiv.)	**8** (10)	40	6		(> 90)	41
8		(2.5 equiv.)	**8** (10)	40	6		(> 90)	41
9		TMSCN	**9** (2)	not indicated	12		(90)	42
10		TMSCN	none	not indicated	24		(0)	42
11		TMSCN	**9** (2)	not indicated	12		(55)	42
12		TMSCN	**9** (2)	not indicated	24		(80)	42

is confirmed by the absence of sorption properties towards nitrogen. According to thermogravimetric analysis (TGA) data, the compound is stable up to 400 °C.

The catalytic properties of compound **9** were also studied in the cyanosilylation and acetalization of carbonyl compounds (see Table 2).[42] Benzaldehyde and acetophenone were used as substrates of cyanosilylation. The reac-

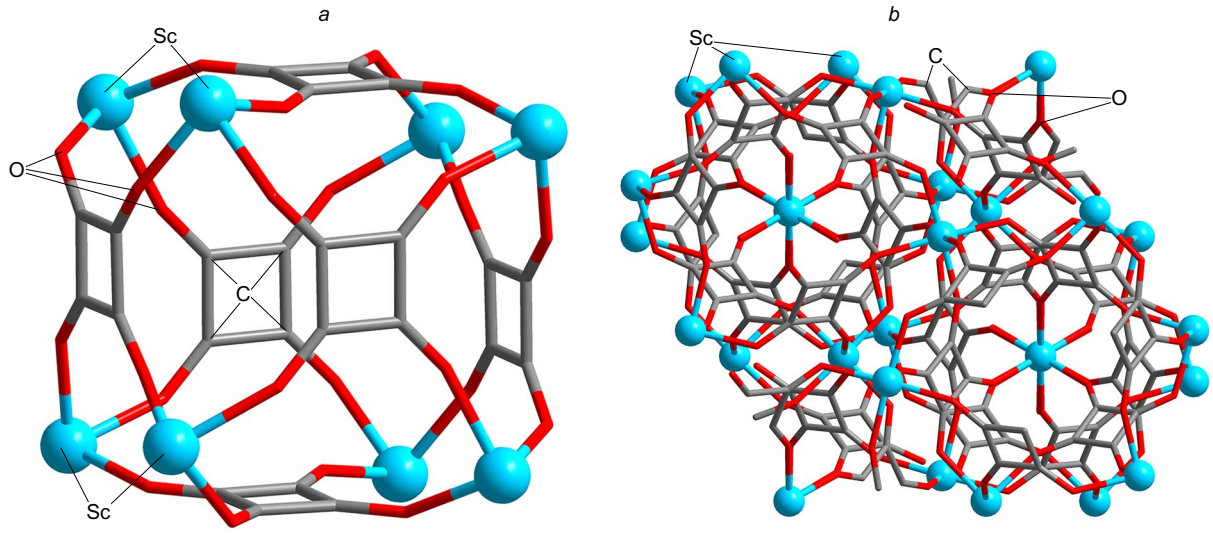


Figure 6. Building block (*a*) and view along the *c* axis (*b*) of the structure of $[Sc_2(squ)_3]$ (**9**).[42]

tions of these substrates with trimethylsilyl cyanide (TMSCN) in the presence of catalyst **9** afforded cyanohydrin trimethylsilyl ethers, which are important industrial intermediates in the production of cyanohydrins, β-amino alcohols, α-hydroxy acids and other biologically active compounds. In the case of benzaldehyde, the conversion was 90% after 12 h, while in the case of acetophenone, the conversions were 55% and 80% after 12 and 24 h, respectively (see Table 2, Nos 9, 11, and 12). In the absence of catalyst **9**, no target product was detected in the reaction mixture containing benzaldehyde and TMSCN even after 24 h (see Table 2, No. 10).

As regards acetalization of aldehydes, scandium squarate (**9**) proved to be a more efficient catalyst than scandium succinate (**8**). At a lower catalyst amount taken {5 mol.% *versus* 8 mol.% used in the case of $[Sc_2(suc)_{2.5}(OH)]$ (**8**)}, acetalization of benzaldehyde with trimethyl orthoformate proceeded in only 1 h with a quantitative product yield (see Table 2, No. 3). In the case of sterically hindered 2-phenylpropionaldehyde, a much longer time (12 h) was required to reach a conversion of 78%; however, catalyst **8** provided only a 65% conversion over the same period of time (see Table 2, Nos 6 and 5, respectively). Like succinate **8**, squarate **9** can be readily recovered and reused for at least 4 times without the loss of selectivity or decrease in the product yield.

2.2. Scandium-organic frameworks with aromatic ligands

Aromatic ligands possess steric rigidity, which increases the framework tolerance to the removal or exchange of guest molecules. Currently, ditopic aromatic carboxylic acids are the most popular bridging ligands for the synthesis of metal-organic, in particular, scandium-organic, frameworks. These ligands may be based on both classical six-membered aromatic rings (Fig. 7) and five-membered heterocycles. A special place among the ligands applied for the synthesis of MOFs is occupied by terephthalic acid (H_2bdc) and its substituted analogues, which combine the steric rigidity, variability of coordination modes and commercial availability. It is not surprising that scandium terephthalates of various structures are currently the most studied SOFs. The

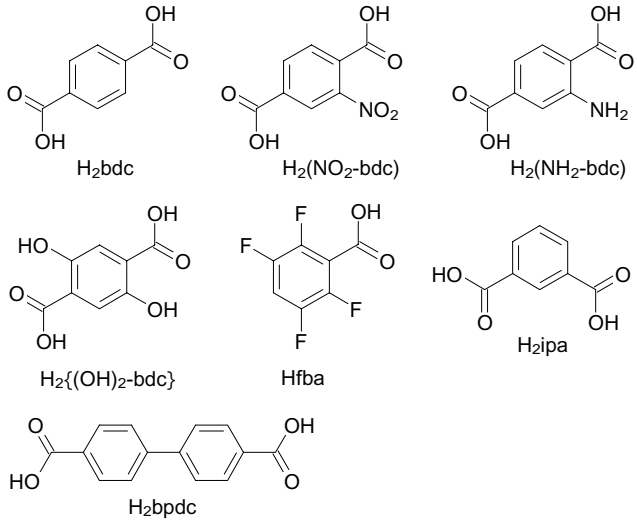


Figure 7. Types of aromatic ligands based on phthalic acids and their derivatives.

structures of SOFs with aromatic ligands presented in published studies often resemble the structures of analogous frameworks based on late lanthanides, which indicates once again the similarity of the coordination chemistry of these metals.

On heating of freshly precipitated scandium hydroxide and tetrafluoroterephthalic acid in methanol, the acid is decarboxylated and the complex $[Sc(fba)_3]$ (**10**) is formed.[43] According to X-ray diffraction data, this compound has a chain structure similar to the structure of scandium acetate (**3**). The polymer chains are linked *via* π–π-interactions between the phenyl groups.

Scandium(III) terephthalate $[Sc_2(bdc)_3]$ (**11**) was obtained by the reaction of scandium acetate hydrate and a mixture of terephthalic acid with sodium terephthalate under hydrothermal conditions in the presence of *o*-phenanthroline (pH 5).[44] Alternative synthetic routes to this MOF

are available from the literature. For example, Mowat *et al.*[45] prepared $[Sc_2(bdc)_3]$ using scandium nitrate trihydrate instead of acetate and without addition of sodium terephthalate or *o*-phenanthroline. However, when the synthesis is conducted under these conditions, the pores of the final product are contaminated with free terephthalic acid and the internal surface area of samples not subjected to additional purification decreases. The structure of **11** is a three-dimensional framework in which each scandium cation is located in an octahedral environment composed of the carboxylate oxygen atoms of six terephthalate anions (Fig. 8 *a*). Each carboxylate group connects two Sc^{III} cations, thus functioning as a bridge and giving rise to chains along the *a* axis (Fig. 8 *b*). These chains are connected by terephthalate bridges along two other directions, thus yielding a three-dimensional structure with 5.4 Å triangular channels extended along the *a* axis and 5×2 Å square channels arranged along the [110] plane (Fig. 8 *c*). Isostructural analogues of compound **11** are also known, namely, $[Sc_2(NO_2\text{-bdc})_3]$ (**12**) and $[Sc_2(NH_2\text{-bdc})_3]$ (**13**), which are prepared by the reaction of scandium oxide (or scandium nitrate in the case of compound **12**) with nitroterephthalic $H_2(NO_2\text{-bdc})$ or aminoterephthalic $H_2(NH_2\text{-bdc})$ acid, respectively, under hydrothermal conditions at 463 K.[45]

Scandium terephthalate $[Sc_2(bdc)_3]$ (**11**) has an exceptionally high thermal stability: according to TGA data, it is stable up to 520 °C. The presence of a porous structure and high stability of coordination polymer **11** and its analogues **12** and **13** are responsible for the interest in more in-depth studies of the functional properties of these frameworks. It was shown that MOF **11** does not catalyze the acetalization of aldehydes, but has high activity and selectivity towards the oxidation of sulfides. In addition, it was shown that scandium terephthalate **11** is a more efficient catalyst than scandium oxide and provides higher conversion and selectivity over the same time period. The catalyst can be easily regenerated and reused for at least 4 times.[44]

Apart from the catalytic properties, scandium terephthalate **11** possesses interesting sorption properties. The N_2 sorption isotherm at 77 K corresponds to type I, which attests to the microporous structure of the compound. According to calculations, the internal surface area (S_{BET}) was 721 $m^2\ g^{-1}$ and the calculated pore size distribution proved the presence of pores 5.5 Å in diameter, which is consistent with X-ray diffraction data. The isotherm of H_2 sorption at 77 K also corresponds to type I and confirms the presence of a microporous structure in the sample with the predominant pore size from 5 to 6 Å.[44] Miller *et al.*[46] carried out a detailed investigation of the sorption properties of compound **11** towards CO_2, CH_4, O_2, CO, N_2, H_2, C_2H_6 and C_3H_8 and determined the crystal structure of the framework loaded with the adsorbed CO_2 (Fig. 9), CH_4, H_2 and C_2H_6 molecules.

It was shown that adsorption of CO_2 at 235 K induces a reduction in the crystal symmetry of MOF **11** from orthorhombic to monoclinic caused by the change in the orientation of terephthalate linkers along the trigonal channels; as a result, these linkers form two types of channels (see Fig. 9).

Upon the sorption of hydrogen at 80 K, the framework symmetry also changes from orthorhombic to monoclinic; however, the authors could not determine the exact position of the hydrogen molecule. Meanwhile, the structure of compound **11** with adsorbed methane and ethane molecules at 230 K retains the orthorhombic symmetry. In the case of methane, the guest molecules are highly disordered and the atomic positions are low-occupied. In the case of ethane, the channels are somewhat expanded and the guest molecules occupy two sites located in the channels and between the ligand benzene rings, respectively. According to the calculated heats of adsorption for the CO_2, CH_4, C_2H_6 and C_3H_8 molecules, the strongest binding in the framework pores is characteristic of CO_2, the binding energy of 23 kJ mol^{-1} being the average value for known frameworks.

A study of the sorption properties of all three compounds **11** – **13** has shown that, although the greatest pore volume is inherent in $[Sc_2(bdc)_3]$ (**11**), the highest sorption capacity with respect to CO_2 at 196 K and low pressure is found for the amino derivative $[Sc_2(NH_2\text{-bdc})_3]$ (**13**), which is due to strong interactions between the ligand amino group and the CO_2 molecule. It is of interest that the CO_2 uptake of $[Sc_2(NO_2\text{-bdc})_3]$ (**12**) at 196 K is also fairly high,

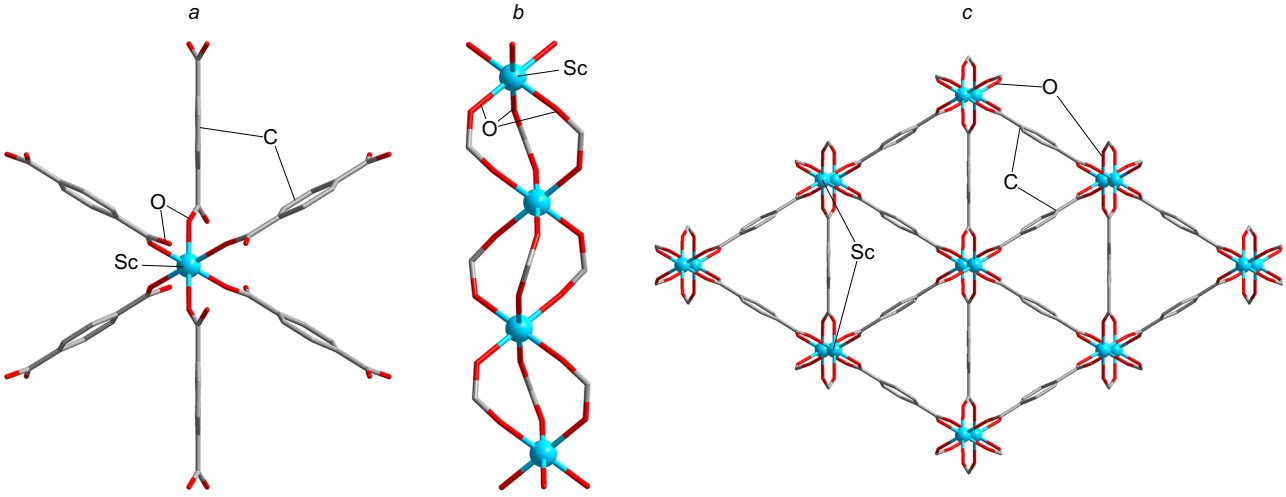


Figure 8. Coordination environment of the scandium ion (*a*) and view of the chain (*b*) and the structure of $[Sc_2(bdc)_3]$ (**11**) along the *a* axis (*c*).[44]

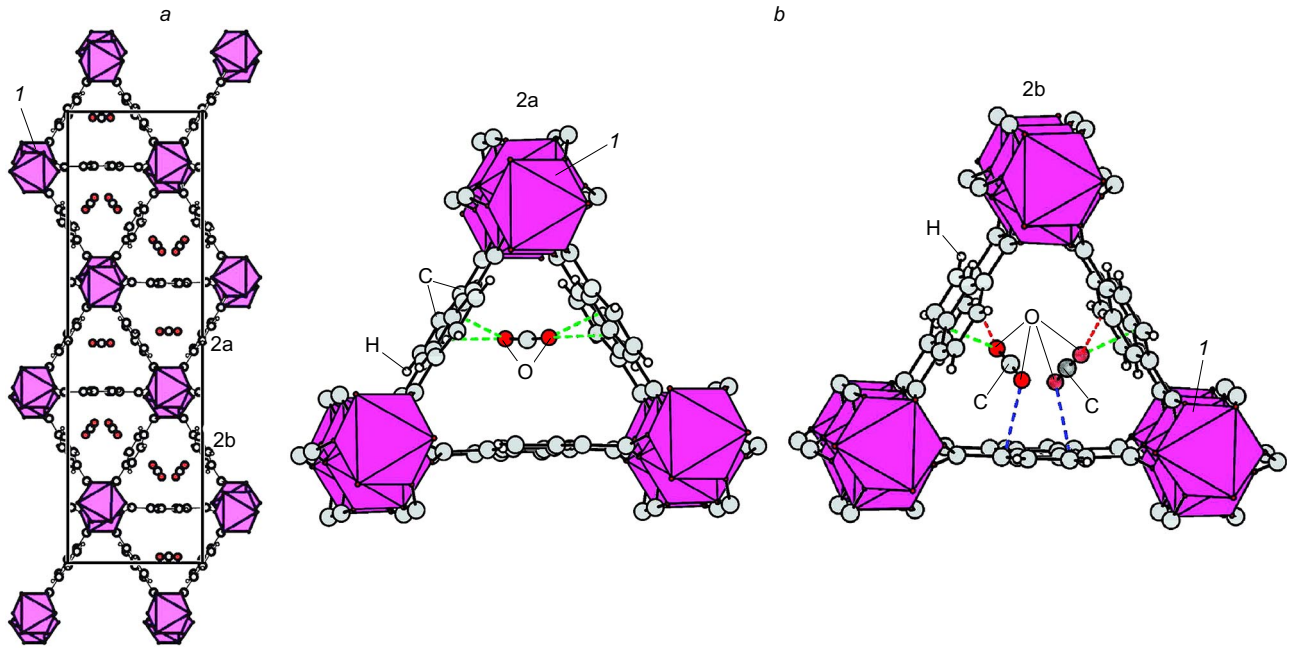


Figure 9. Schematic representation of the CO_2 adsorption sites in the 2a and 2b type channels of compound $[Sc_2(bdc)_3]$ (**11**) (*a*) and detailed scheme of the adsorption sites in 2a and 2b type channels (*b*).[46]
(*1*) Scandium coordination polyhedra.

as the NO_2 groups of the ligand can rotate thus allowing the gas molecules to move along the narrow channels. The sorption measurements and Monte Carlo and density functional theory (DFT) calculations of the efficiency of selective CO_2 sorption from CO_2-CH_4 and CO_2-N_2 mixtures for the series of isostructural microporous frameworks **11**–**13** demonstrate that MOF **12** is a highly selective sorbent with respect to CO_2. The selectivity factors calculated for CO_2-N_2 and CO_2-CH_4 mixtures are 1050 and 4000, respectively, at 303 K and 1 bar, being superior to those for most of the known MOFs and other porous materials.[47]

As noted above, upon sorption of CO_2 at 235 K, framework **11** crystallizes in the monoclinic system,[46] while according to a more recent publication of Mowat *et al.*,[45] the empty scandium(III) terephthalate framework should crystallize in the orthorhombic system. In order to clarify the mechanism of interaction of CO_2 molecules with the framework, the authors carried out Monte Carlo calculations for two framework polymorphs at 235 K. It was shown that the structure of scandium terephthalate $[Sc_2(bdc)_3]$ is flexible and the tilt angle and the plane of terephthalate ligands in the unit cell can be adjusted to optimize the position of the CO_2 molecule in different sorption sites.[45] Miller *et al.*[46] found that sorption of methane, ethane and propane molecules does not cause symmetry changes of this type and the structure remains orthorhombic. It is of interest that in the case of substituted derivatives $[Sc_2(NH_2\text{-bdc})_3]$ (**13**) and $[Sc_2(NO_2\text{-bdc})_3]$ (**12**), no symmetry changes take place on going from the empty framework to the CO_2-loaded one, which may be attributable to steric restrictions in the frameworks with substituted ligands.[45]

Greenaway *et al.*[52] employed IR spectroscopy to investigate the interaction of CO_2 molecules with the framework $[Sc_2(NH_2\text{-bdc})_3]$ (**13**). According to *in situ* powder X-ray diffraction, at 298–273 K and a CO_2 pressure of 0.1 bar, the structure retains the orthorhombic group of symmetry. The heat of adsorption of CO_2 in MOF **13** calculated from X-ray diffraction data is 31 ± 2 kJ mol^{-1}, which corresponds to the isosteric heat of adsorption of 31 ± 3 kJ mol^{-1} calculated from sorption isotherms at different temperatures. The heats of adsorption for MOF **13** are markedly higher than those for MOF **11** (23 kJ mol^{-1}), which is accounted for by the interaction between CO_2 molecules and the amino group of MOF **13**.

Sotelo *et al.*[48] described an approach to filling the channels of the framework $[Sc_2(bdc)_3]$ (**11**) with gas molecules at high pressure, which comprises the use of liquefied gases and a diamond anvil cell. Loading of MOF **11** with liquefied CO_2 at 2 kbar revealed the presence of a new, previously unknown adsorption site for gas molecules (site *3*, Fig. 10) and resolved previous inconsistencies between structural data and adsorption isotherms. Proceeding from the new structural data, the authors calculated the maximum theoretical CO_2 uptake to be 6.2 mmol g^{-1}, which is much closer to the experimental value of 6.5 mmol g^{-1} (Ref. 47) than the value calculated previously (3.4 mmol g^{-1}). According to the results of measurements with supercritical CH_4 in the pressure range of 3–25 kbar, two reversible phase transitions accompanied by a decrease in the overall system volume take place in compound **11** hyperfilled with the gas (Fig. 11).

A study of the structural changes and phase transitions in scandium(III) terephthalate framework **11** over a broad temperature range (from 140 to 523 K) by synchrotron X-ray powder diffraction demonstrated the presence of a phase transition from the monoclinic (*C*2/*c*) to the orthorhombic (*Fddd*) system at 225 K.[45] The orthorhombic polymorph shows negative thermal expansion and, according to Rietveld analysis, this largely results from compression along the *c* axis caused by rotation of the carboxylate

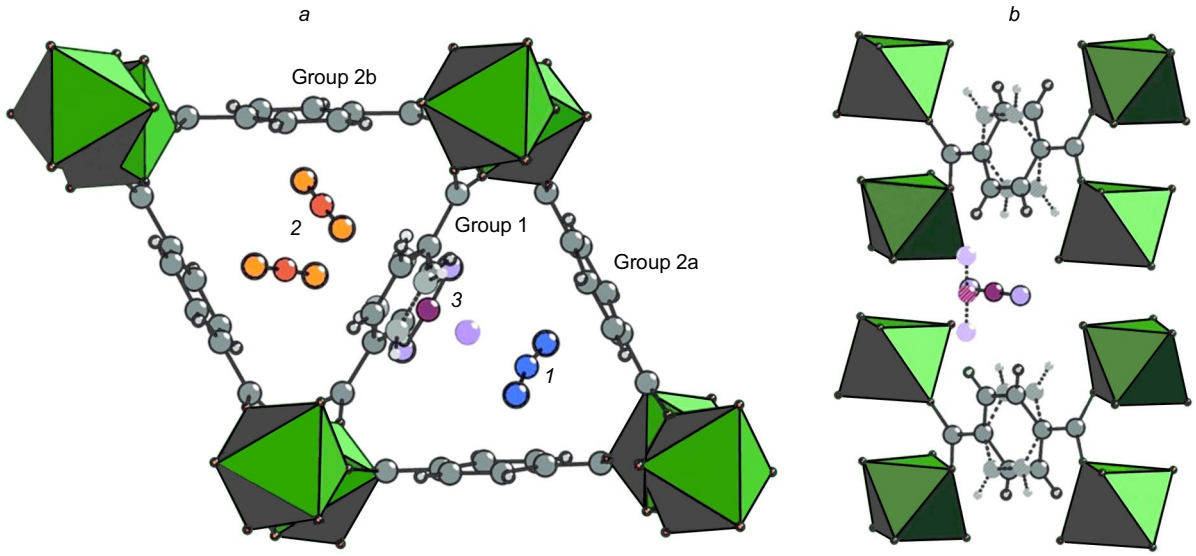


Figure 10. Arrangement of CO_2 adsorption sites (*1*, *2*, *3*) in the channels formed by symmetrically independent linkers (groups 1, 2a and 2b) in the framework $[Sc_2(bdc)_3]$ (**11**) (*a*) and disorder schemes for site *3* and the bdc-linker of group 1 (*b*).[48]

groups and displacement of the aromatic rings (Fig. 12). The solid-state NMR data for deuterated $[Sc_2(D_4\text{-bdc})_3]$ indicated reorientation of the benzene rings at 298 K. A similar investigation of deuterated monosubstituted derivatives **13** at 100 and 298 K and of **12** at 100, 298, 373 and 473 K demonstrated that frameworks **12** and **13** do not change their symmetry in the indicated temperature range. The retention of the orthorhombic system of $[Sc_2(NH_2\text{-bdc})_3]$ (**13**) with temperature rise is attributable to the stabilizing interactions between the hydrogen atoms of the amino group and the oxygen atoms of the ligand carboxyl, while the retention of the monoclinic symmetry of $[Sc_2(NO_2\text{-bdc})_3]$ (**12**) is due to steric restrictions created by the nitro group.

Studies of the structural changes in frameworks $[Sc_2(bdc)_3]$ (**11**) and $[Sc_2(NO_2\text{-bdc})_3]$ (**12**) at high pressure (0.1 – 2.3 GPa) in the presence of non-penetrative (Fluorinert-77 perfluorinated solvent) or sorbable (methanol)

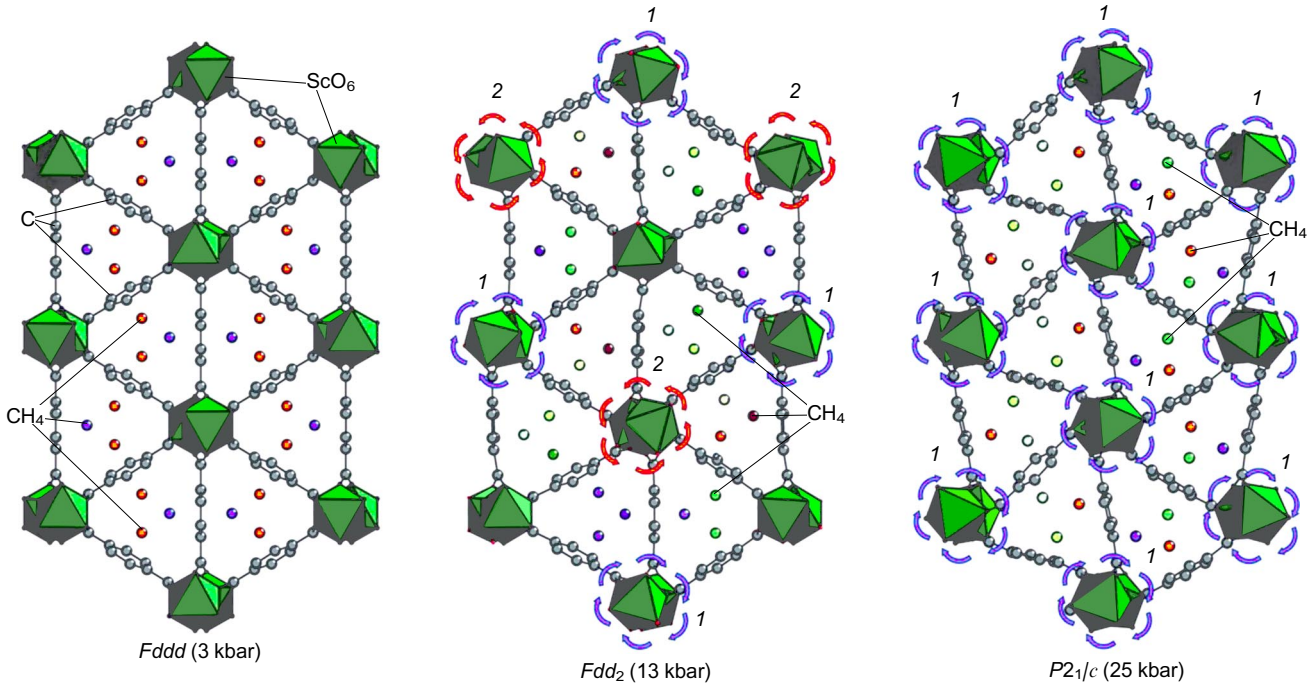


Figure 11. Scheme of successive structural transitions of $[Sc_2(bdc)_3]$ (**11**) during pore filling with methane molecules at elevated pressure.[48] CH_4 are methane molecules situated in different adsorption sites. (*1*) Clockwise and (*2*) counter-clockwise rotation of the ScO_6 octahedra in each phase.

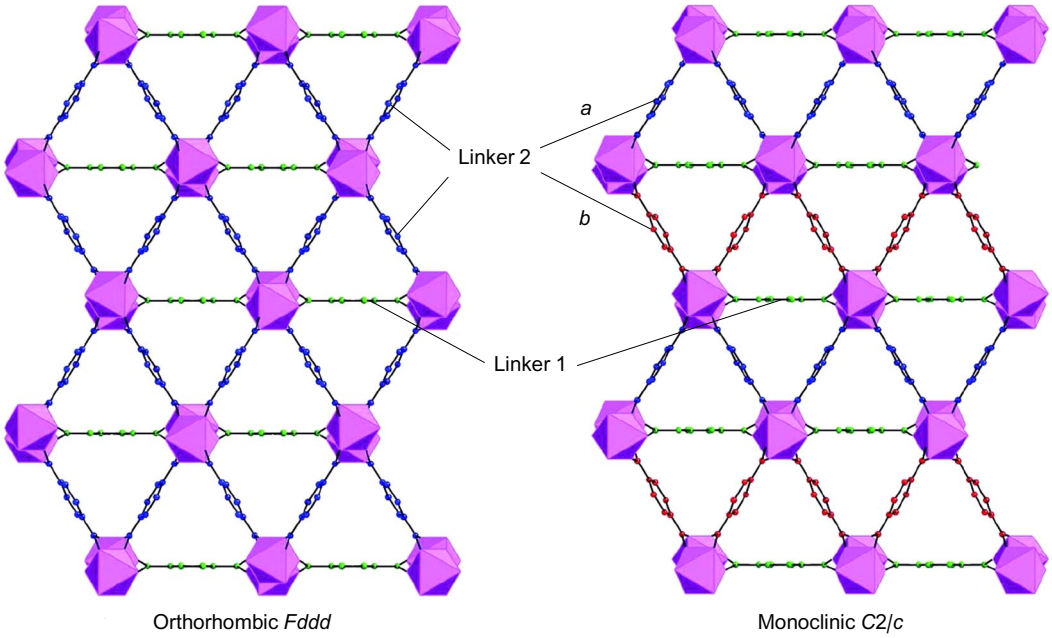


Figure 12. Comparison of the orthorhombic (*Fddd*) and monoclinic (*C*2/*c*) models for the structure of compound $[Sc_2(bdc)_3]$ (**11**).[45] *a* and *b* are non-equivalent linkers in the monoclinic structure.

hydrostatic fluids showed that MOF **11** immersed into Fluorinert-77 undergoes reversible amorphization at 0.1 GPa, whereas MOF **12** undergoes monoclinic (*C* 2/*c*) to orthorhombic (*Fdd*2) phase transition.[49] Conversely, in the presence of methanol, neither amorphization of framework **11** nor phase transitions of framework **12** take place up to 3 GPa. It was shown by both experimental and theoretical methods that the stabilizing effect of methanol is caused by incorporation of methanol guest molecules into the frameworks with the formation of intermolecular hydrogen contacts.

McKellar *et al.*[50] reported a new procedure for increasing the efficiency of CO_2 sorption by the framework $[Sc_2(bdc)_3]$ with the use of perfluorinated Fluorinert-77. During the experiment, carbon dioxide dissolved in Fluorinert-77 penetrates into the crystal under the liquid pressure. It was noted that the liquid pressure-induced incorporation of guest molecules is suitable for studying the 'breathing' effects in the flexible frameworks and can serve as a convenient method for estimation of the real gas storage capacity of the material, because the experiments are carried out at room temperature rather than at a low temperature, which is the case for most sorption experiments. Thus using the proposed approach, the same authors were able to force the bulky C_5-C_8 alkane molecules into the voids of microporous scandium terephthalate **11** at high pressure (up to 0.8 GPa) (Fig. 13).[51] The uptake of these guests resulted in reorientation of aromatic rings of one-third of terephthalate linkers in structures **11**. The linkers acted as 'torsion springs' and thus induced reversible change in the local pore structure. The fact that framework **11** responded in different ways to the inclusion of linear and mono-, di- and tribranched hydrocarbons indicated the possible applicability of this porous material for separation of hydrocarbons. In particular, only linear molecules are adsorbed by the framework under ambient conditions,

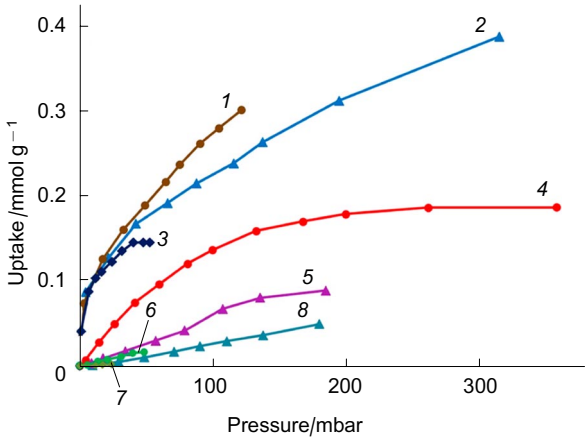


Figure 13. Sorption isotherms of various hydrocarbons at 298 K for $[Sc_2(bdc)_3]$ (**11**).[51]
(*1*) n-Hexane, (*2*) n-pentane, (*3*) n-heptane, (*4*) 2-methylbutane, (*5*) 2,3-dimethylbutane, (*6*) 2,2,4-trimethylpentane, (*7*) 2-methylheptane, (*8*) 2,2-dimethylbutane.

while monobranched hydrocarbons can penetrate only at elevated pressure.

The scandium(III) oxo-terephthalate $\{[Sc_3O(bdc)_3(H_2O)_3]\cdot 0.5\,Cl\cdot 0.5\,(OH)\cdot 4\,(DMF)\ 3\,(H_2O)\}$ (**14**) was prepared[53] under solvothermal conditions by the reaction of scandium chloride hydrate with terephthalic acid in a slightly acidified solvent mixture (dimethylformamide, 1,4-dioxane, water).[53] Alternative methods for the synthesis include heating of scandium nitrate trihydrate with terephthalic acid in dimethyl- or diethylformamide.[54] Compound **14** is a full structural analogue of the known chromium(III) oxo-terephthalate $[Cr_3O(bdc)_3(H_2O)_3]$ (MIL-88).[84]

Preparation of the dihydroxy-substituted derivative $[Sc_3O\{(HO)_2\text{-bdc}\}_3(H_2O)_3(NO_3)]$ (**15**)[55] by the reaction of 2,5-dihydroxyterephthalic acid ($H_2\{(HO)_2\text{-bdc}\}$) with scandium nitrate or chloride in a DMF – ethanol – H_2O mixture under solvothermal conditions has been reported.

The structures of the above-described compounds are based on trinuclear oxo-carboxylate complexes like $\{M_3O(RCOO)_6(H_2O)_3\}$, which are well-known in the classical coordination chemistry of many transition metals. In these complexes, three metal cations are connected by the bridging oxo-anion located at the centre of the 'metal triangle' and are also connected in pairs by six bridging carboxylate ligands (Fig. 14). In addition, each metal cation has one more site occupied by the coordinated solvent molecule and, hence, the metal coordination environment turns into a distorted octahedron.

In compound **14**, these complexes function as secondary building blocks with a trigonal-prismatic geometry; they are connected by terephthalate bridges into a three-dimensional framework with a nickel arsenide topology (Fig. 15). The structure has hexagonal channels 7.6 Å in diameter, which are interconnected with narrower windows approximately 3.5 Å in diameter. The free void volume is ~60%.

Like many other SOFs, framework **14** has a high thermal stability. According to *in situ* powder X-ray diffraction data, compound **14** retains the crystallinity at elevated temperature up to 350 °C, while according to IR spectroscopy data, the coordinated water molecules are eliminated under these conditions. Like in the case of chromium(III) oxo-terephthalate MIL-88 described previously, the structural dynamics of porous framework **14** depends on the presence of guest molecules in the cavities and the degree of activation and involves the change in the unit cell parameters.[85] Therefore, the sorption properties of compound **14** depend appreciably on the sample prehistory, activation procedure and conditions of experiments. The permanent porosity of activated scandium(III) oxo-terephthalate framework **14** was confirmed by measurements of N_2 adsorption isotherms, which have type I shape corresponding to microporous adsorbents. The BET internal surface area is 634 $m^2\ g^{-1}$. The H_2 adsorption isotherms are fully reversible and their shape is also typical of microporous compounds. The heat of adsorption of H_2 at zero coverage was 5.25 kJ mol^{-1}, which is typical of most porous MOFs without exposed metal sites.[86]

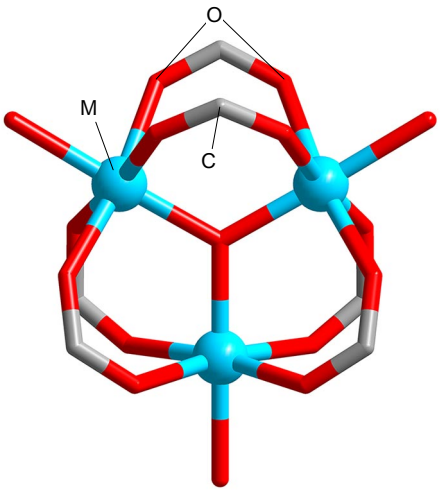


Figure 14. Structure of the $\{M_3O(RCOO)_6(H_2O)_3\}$ building block.[53]

Mitchell *et al.*[56] prepared an isoreticular analogue of scandium(III) oxo-terephthalate with a diphenyl-4,4′-dicarboxylic acid (H_2bpdc) ligand with the formula $\{[Sc_3O(bpdc)_3(H_2O)_3](OH)\}$ (**16**). An increase in the length of the organic ligand results in a pronounced increase in the pore diameter and in the proportion of voids in the MOF. Like other analogues, $[Sc_3O(bpdc)_3(H_2O)]$ has some structural flexibility. Despite the large pore size, sorption measurements show a moderate capacity of the framework for nitrogen (0.47 ml g^{-1}); the authors attributed this result to interpenetration of two frameworks. Neither of the isoreticular compounds, $\{[Sc_3O(bdc)_3(H_2O)_3]\cdot 0.5\,Cl\cdot 0.5\,(OH)\cdot 4(DMF)\cdot 3\,(H_2O)\}$ (**14**)

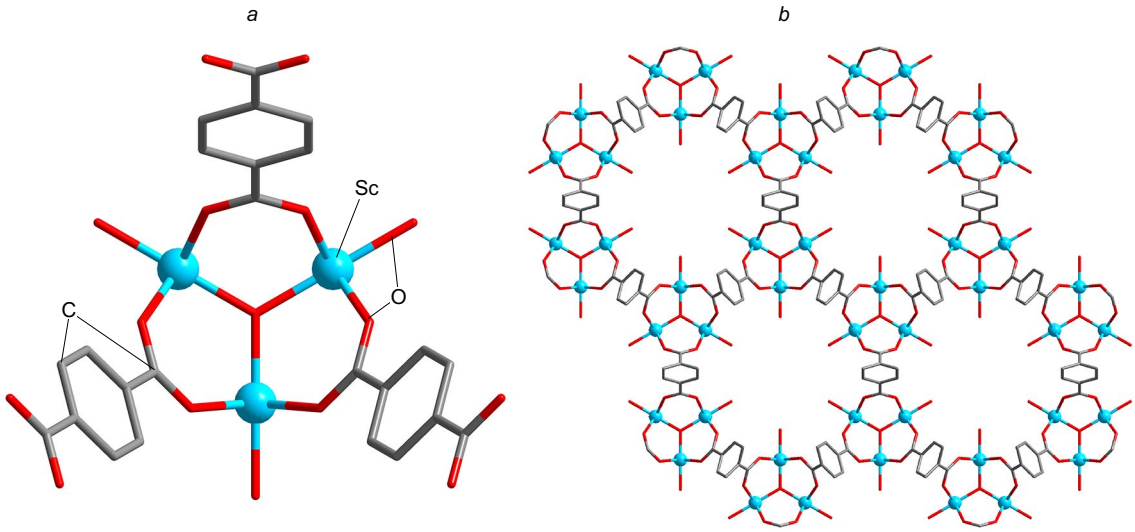


Figure 15. Building block (*a*) and view along the *c* axis of the structure of $\{[Sc_3O(bdc)_3(H_2O)_3]\cdot 0.5\,Cl\cdot 0.5\,(OH)\cdot 4\,(DMF)\cdot 3\,(H_2O)\}$ (**14**) (*b*).[53]

and {[$Sc_3O(bpdc)_3(H_2O)_3$](OH)} (**16**), containing terephthalic and diphenyldicarboxylic acids, respectively, showed a noticeable catalytic activity towards the reaction of nucleophilic alkenes with electron-deficient aldehydes or the Friedel–Crafts reaction between a substituted indole and electron-deficient alkenes, which may be due to the impeded access of reactants to the Sc^{III} active sites due to the coordination of water molecule.

Scandium(III) hydroxy-terephthalate [Sc(OH)(bdc)] (**17**)[56] is a structural analogue of another known vanadium(III)-containing framework — MIL-68.[87] Coordination polymer **17** is composed of chains consisting of the {ScO_6} octahedra, in which bridging hydroxy groups (μ_2-OH) are located in the *trans*-positions. The octahedra are connected in pairs by two bridging carboxyl groups of the terephthalate anions (Fig. 16). In the crystal structure of **17**, the chains are arranged parallel to one another and are connected by terephthalate bridges, thus forming a hexagonal channel structure with a maximum channel diameter of ~20 Å. The adsorption measurements demonstrated that the pore volume of 0.1 ml g^{-1} determined using N_2 adsorption is much lower than that for known structural analogues {for example, the pore volume for [Ga(OH)(bdc)] is 0.46 cm^{-3} g^{-1} (Ref. 88)}. Nevertheless, compound **17** adsorbs a substantial amount of CO_2 (14 mmol g^{-1}) at 196 K and the pore volume determined from carbon dioxide adsorption data (0.59 cm^3 g^{-1}) proved to be much higher than that calculated from nitrogen adsorption isotherms. Catalytic experiments demonstrated that this compound is a moderately efficient catalyst of reactions between nucleophilic alkenes and electron-deficient aldehydes and the Friedel–Crafts reaction between the substituted indole and methyl vinyl ketone. The moderate efficiency of MOF **17** was attributed to the absence of coordinatively unsaturated metal sites and partial pore blocking, which is consistent with the results of sorption experiments.[56]

A topological isomer of scandium(III) hydroxy-terephthalate **17** with rhombic channels was prepared by the research team of Professor Mowat.[54] The compound [Sc(OH)(bdc)] (**18**) was synthesized by the reaction of scandium nitrate trihydrate with terephthalic acid in dimethylformamide at 463 K. Under similar conditions but using mononitroterephthalic acid, the corresponding nitro derivative [Sc(OH)(NO_2-bdc)] (**19**) is formed.[45] The crystal of **18** is fully analogous to that of the chromium(III)-based framework MIL-53 synthesized by Professor Ferey's research team in 2002.[89] Like MOF **17**, the coordination structures of **18** and **19** are composed of chains of the {ScO_6} octahedra with bridging hydroxide and carboxylate anions. The difference is only in the mode of linking of these chains by organic anions into a three-dimensional framework and, correspondingly, in the shape of channels (see Fig. 16). According to TGA data, compound **18** is stable below 723 K.

It is known that the chromium analogue, MIL-53 [Cr(OH)(bdc)], exhibits a marked framework 'breathing' behaviour depending on the sample activation method; this affects the sorption characteristics of the material.[90,91] Similar effects were detected for compound **18** in a study of its sorption properties.[57] The completely desolvated framework does not adsorb N_2. At 196 K, compound **18** has a noticeable sorption capacity with respect to CO_2 (13.2 mmol g^{-1}), and the sorption and desorption curves form a hysteresis associated with structural changes and

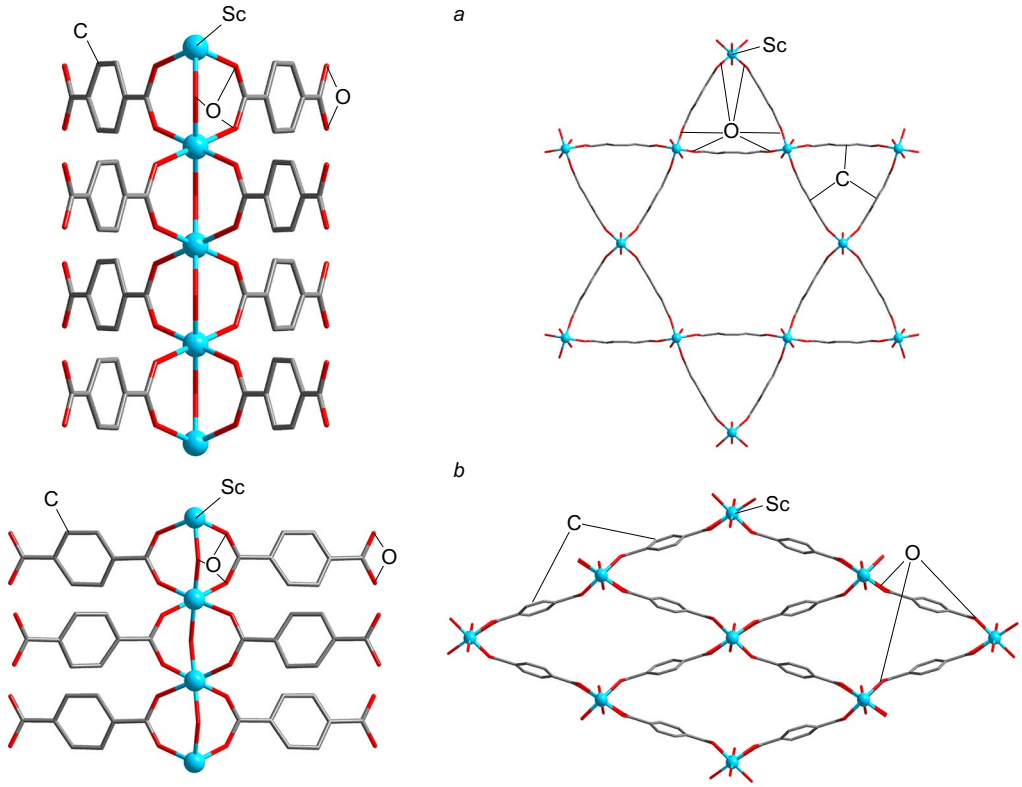


Figure 16. Structure of the chains and view across the channels for the topological isomers [Sc(OH)(bdc)] (**17**) (*a*) and **18** (*b*).[45,54]

transitions between the open- and closed-pore states of the framework ('breathing') in response to the change in CO_2 pressure. The structural dynamics of framework **18** at different temperatures (100 – 623 K) and CO_2 pressures of 0 – 0.9 bar (196 K) was interpreted and described using theoretical calculations, which were confirmed by *in situ* powder X-ray diffraction.

A study of the dependence of the structural changes in the framework on the nature of the metal site and functional substituents in the ligands for a series of MIL-53 derivatives [M(OH)(X-bdc)] (M = Al, Cr, Fe, Sc; X = Cl, Me, NO_2) at elevated pressure demonstrated that the scandium compound does not undergo the monoclinic to triclinic transition over a whole pressure range studied, unlike the coordination polymers based on Al, Cr and Fe; the pressure of this transition depends on the nature of the metal.[58]

Lian *et al.*[59] used the procedure for the synthesis of compound **18** (Ref. 54) as the base for the preparation of a new MIL-53 analogue with a mixture of terephthalic and isophthalic acids. The obtained crystalline powder was placed into an ethanol solution of europium(III) nitrate. The final composite material containing europium cations served for fluorescence determination of benzoylacetic acid, a biological marker of styrene and polystyrene. It was shown that this composite is a rare example of a 'turn-on' luminescent sensor for rapid determination of small amounts (down to ppm) of benzoylacetic acid in urine and blood serum.

Zeolite-like scandium(III) oxo-terephthalate $[Sc_3O(bdc)_3(H_2O)_3(OH)]$ (**20**) was prepared by the reaction of scandium nitrate with the acid in dimethyl- or diethylformamide at 393 – 423K.[60] The framework is based on trinuclear oxo-carboxylate complexes connected by terephthalic acid residues to give tetrahedral patterns in which the trinuclear $\{Sc_3O(RCOO)_6(H_2O)_3\}$ moieties (see Fig. 14) are tetrahedron vertices, while the terephthalate anions are edges. These tetrahedral building units are connected through vertices to form a MTN type zeolite-like structure with very large internal voids up to 3.4 nm in diameter. The structure of compound **20** is fully identical to that of chromium(III) oxo-terephthalate $[Cr_3O(bdc)_3(H_2O)_3]$ (MIL-101) (Fig. 17), which is a well-known porous framework.[92] Measurements of N_2 sorption by a thermally activated sample of compound **20** attest to a microporous structure of the compound, although the pore volume (0.16 $cm^3\ g^{-1}$)[56] is much lower than expected and than that found for MIL-101 (2.0 $cm^3\ g^{-1}$),[93] which may be caused by partial blockage of the pores during thermal activation. Measurements of the N_2 sorption by a sample of **20** activated without heating showed internal surface area of up to 2800 $m^2\ g^{-1}$.[60] This is comparable with, but is still markedly lower than the value found for MIL-101 (4100 $m^2\ g^{-1}$).[93] Mitchell *et al.*[56] studied the catalytic properties of compound **20** towards various reactions catalyzed by Lewis acids such as the reactions of nucleophilic alkenes with electron-deficient aldehydes, the Friedel – Crafts reaction between the heterocyclic compounds and electron-deficient alkenes and reactions of ketimine and aldimine formation. Compound **20** showed a moderate catalytic activity, which is apparently due to insufficient framework stability under the reaction conditions.

Apart from mono- and dicarboxylate bridging ligands, sterically rigid aromatic ligands with three or four carboxylate groups are also rather popular in the chemistry of MOFs (Fig. 18). The use of these ligands results in compounds with more complex topology and, most often, more structurally rigid frameworks.

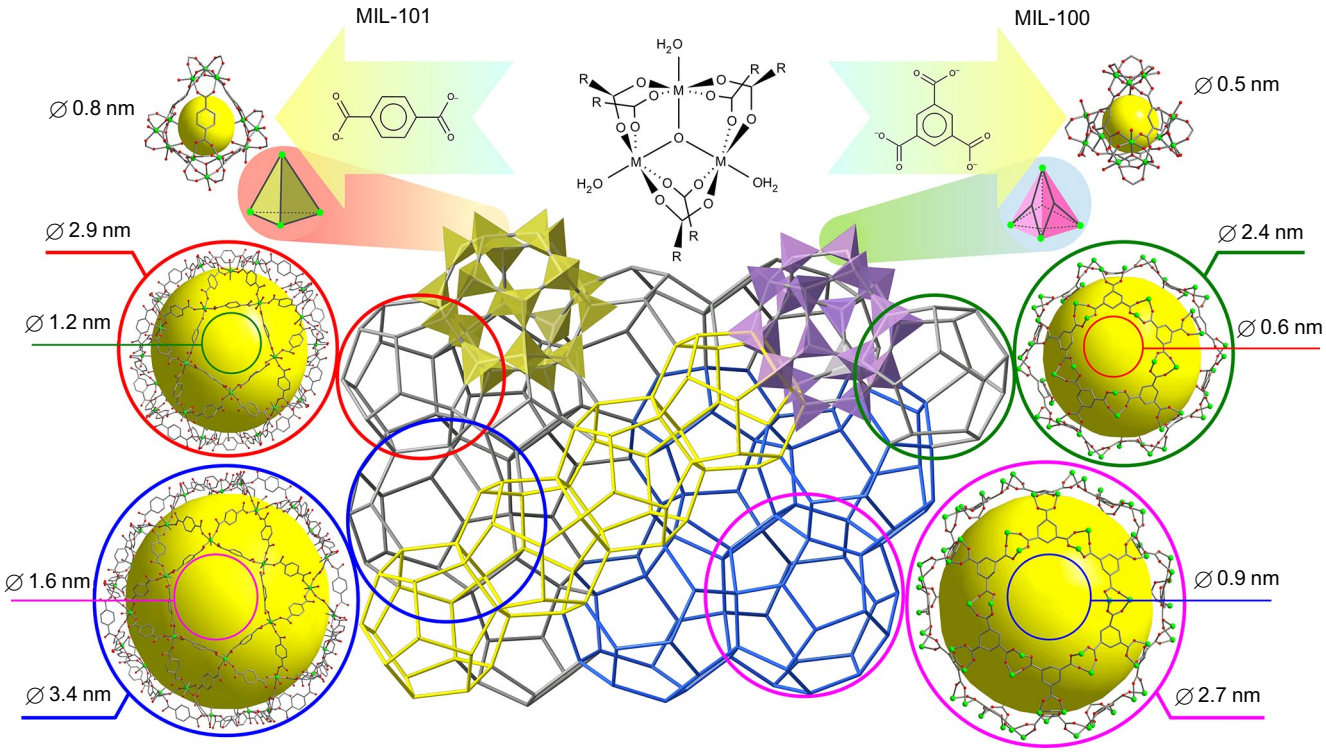


Figure 17. Schematic structure of MIL-100 and MIL-101.[92, 93]

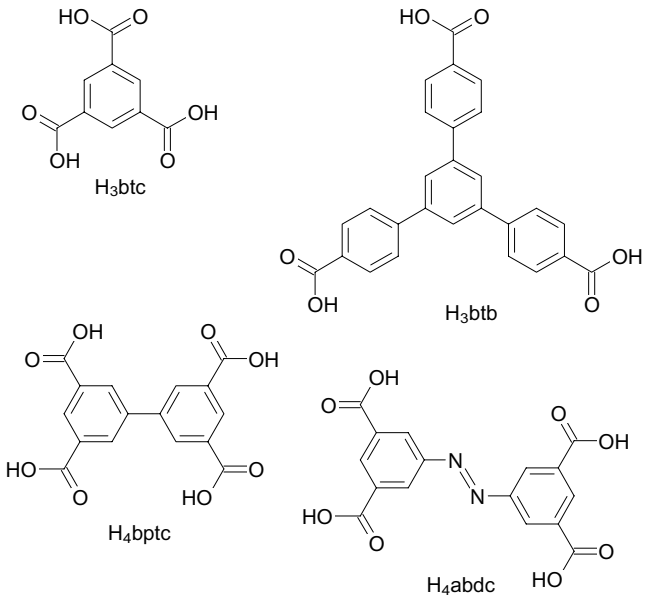


Figure 18. Types of aromatic ligands with three or four carboxylate groups.

The synthesis of SOF with trimesic acid (H_3btc) afforded scandium(III) oxo-trimesate $[Sc_3O(btc)_2(H_2O)_3(OH)]$ (**21**), which is composed of the above-described (see Fig. 14) trinuclear oxo-carboxylate complexes connected by trimesic acid residues.[54] Compound **21** was obtained as a crystalline powder by the reaction of scandium nitrate with trimesic acid in DMF at 373 K. The structure of this product is fully identical to the structure of chromium(III) oxo-trimesate $[Cr_3O(btc)_2(H_2O)_3(OH)]$ (MIL-100) (see Fig. 17)[93] and also resembles the structure of framework **20**, *i.e.*, it is composed of tetrahedral moieties in which the trinuclear secondary building blocks $\{Sc_3O(RCOO)_6(H_2O)_3\}$ are tetrahedron vertices and the trimesate anions are tetrahedron faces. The tetrahedral building blocks are connected *via* the vertices to give an MTN type zeolite-like structure with large inner voids up to 3.0 nm in diameter, which allows this compound to be classified as a mesoporous material. The N_2 sorption isotherm for MOF **21** is a two-step curve, which is in line with the micro-mesoporous nature of the material. The N_2 uptake is 27 mmol g^{-1} at 77 K and the CO_2 uptake is 21.34 mmol g^{-1} at 195 K.[54] The maximum internal surface area determined by the BET method is 1400 m^2 g^{-1} (Ref. 56), which is lower than that of MIL-100 (3100–4230 m^2 g^{-1}).[94]

Studies of aluminium, chromium, iron and other metal analogous of the MIL-101 framework and the high porosity and chemical stability found for SOFs **20** and **21** resulted in the appearance of publications giving detailed descriptions of the functional properties of these compounds, first of all, the sorption and catalytic properties.[95–98] In addition, the sorption and catalytic properties of $[Sc_3O(btc)_2(H_2O)_3(OH)]$ (**21**) and bimetallic compounds $[(Sc_{3-x}M_xO(btc)_2(H_2O)_3]$ (M = Al, Cr, Fe) were studied by different research teams all over the world.[56,61–65]

The interaction of adsorbed H_2 molecules with coordinatively unsaturated metal sites in scandium(III) oxo-trimesate **21** was studied by IR spectroscopy.[61] The authors calculated the enthalpy and entropy of adsorption, which were -11.2 kJ mol^{-1} and -120 J mol^{-1} K^{-1}, respectively. Gallis *et al.*[62] elucidated the causes behind the O_2/N_2 sorption selectivity of MOF **21**. Using Monte Carlo and DFT calculations, they showed that the selectivity is associated with internal distortions in the framework in which the adsorbed O_2 molecules interact with metal sites particularly in the tetrahedral cages and induce changes in the unit structure. The O_2 sorption was found to be reversible and cyclable for at least 10 cycles without additional activation between the cycles and without the loss of gas uptake (Fig. 19).

Mitchell *et al.*[56] investigated the catalytic properties of scandium(III) oxo-trimesate **21** towards the formation of C–C and C=N bonds in Lewis acid-catalyzed reactions such as the reaction of nucleophilic alkenes with electron-deficient aldehydes, the Friedel–Crafts reaction between heterocyclic compounds and electron-deficient alkenes, and ketimine and aldimine formation reactions. In each of these reactions, MOF **21** acted as an active and selective heterogeneous catalyst, most often providing product yields above 90%. Almost in all cases, the scandium-based framework was more efficient than the isostructural analogues based on other trivalent metals and more efficient than other scandium(III)-based frameworks.[40,41,44]

A comparison of the textural, acidic and catalytic characteristics of compound **21** and the isostructural $[M_3O(btc)_2(H_2O)_3]$ (M = Al, Cr, V) by means of IR spectroscopy indicated that the acidity of active sites decreases in the series Al > Cr > V > Sc.[63] The catalytic activity of the frameworks was studied for the methanol or propan-1-ol addition reaction to 3,4-dihydro-2*H*-pyran. In the case of $[Sc_3O(btc)_2(H_2O)_3]$, the product yield was 100% for methanol, whereas for propan-1-ol, the yield was only 25% at room temperature and 80% at 333 K. In addition, the catalytic properties of $[M_3O(btc)_2(H_2O)_2(OH)]$ (M = Al, Cr, Fe, In, Sc, V) were studied for the Prins condensation, which was used as the model reaction.[64] According to IR spectroscopy data, the acidity of active sites decreased in the series Al > Cr > V > In ≈ Fe > Sc. All frameworks were found to show 100% selectivity to nopol in the reaction of β-pinene with formaldehyde. The highest yields (>90% after a 20 min reaction) were provided by the V- and Sc-based frameworks; generally, the catalyst efficiency decreased in the series V > Sc ≫ Fe > Al > Cr > In, which is in line with the experimentally determined numbers of accessible metal active sites in the series of isostructural frameworks.

The catalytic activity of mixed-metal frameworks $[Sc_{3-x}M_xO(btc)_2(H_2O)_3]$ (M = Al, Cr, Fe) structurally similar to SOF **21** towards the tandem formation of C–C bonds and oxidation of alcohols was found to increase with increasing scandium content in the framework, while the attenuating effect of the second metal in the framework decreased in the series Al > Fe > Cr.[65]

Compound **22** with the formula $[Sc_3O(btb)_2(H_2O)_3(OH)]$ [H_3btb is 1,3,5-tris(4-carboxyphenyl)benzene] can be prepared by solvothermal reaction of scandium chloride hydrate with H_3btb in an acidified solvent mixture (DMF–THF–CH_2Cl_2–H_2O).[53] According to X-ray diffraction data, like compounds described above, compound **22** is composed of trinuclear secondary building blocks $\{Sc_3O(RCOO)_6(H_2O)_3\}$ (see Fig. 14), but its topology differs from the MIL-100 topology, which is

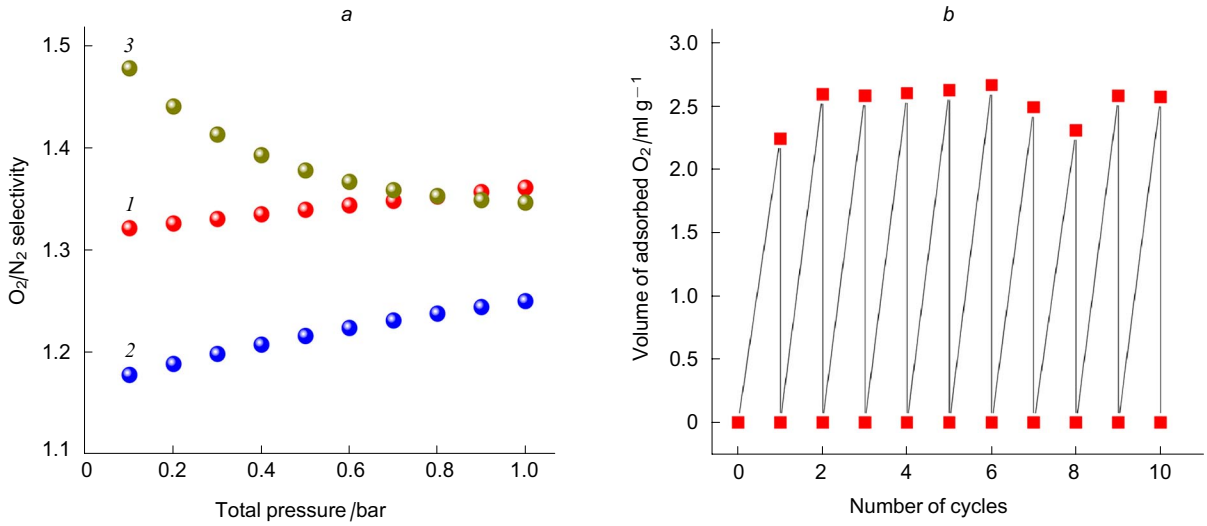


Figure 19. O_2/N_2 sorption selectivity calculated by the ideal adsorbed solution theory (IAST) method for the framework Sc-MIL-100 at temperatures of 258 (*1*), 298 (*2*) and 313 K (*3*) (*a*) and cyclability of the O_2 sorption – desorption by $[Sc_3O(btc)_2(H_2O)_3(OH)]$ (**21**) (*b*).[62]

encountered in MOF **21**. In compound **22**, each trinuclear building block is connected to 12 neighbouring blocks through six btb^{3-} bridging ligands, thus forming a highly porous structure containing channels 23 Å in diameter (Fig. 20). Coordination polymer **22** has a high thermal stability: *in situ* powder X-ray diffraction at elevated temperature showed that the crystallinity is retained up to 350 °C. Using IR spectroscopy, the authors[53] also found that the coordinated water molecules cannot be eliminated from the freshly synthesized compounds under these conditions. However, unlike compound **14**, in the case of **22**, the replacement of guest molecules by acetone makes it possible to completely eliminate the coordinated water molecules even at 250 °C.

Also, the sorption properties were studied for activated sample **22** obtained by direct heating of freshly prepared material (sample **22a**) and the sample obtained by replacement of guest molecules by acetone followed by heating (sample **22b**). Irrespective of the activation procedure, the sorption isotherms had steps, although according to results of calculations, the isotherm corresponds to type I inherent in microporous sorbents. The calculated specific internal surface areas S_{BET} were 1233 and 1511 $m^2\ g^{-1}$ for **22a** and **22b**, respectively. It is of interest that the multistage activation of the framework not only enhances the porosity, but also considerably increases the heat of adsorption of H_2 molecules at zero pressure. Indeed, the enthalpy of hydrogen adsorption proved to be 2.59 kJ mol^{-1} for sample **22a** and 6.90 kJ mol^{-1} for sample **22b**. The considerable increase in the heat of adsorption is associated with the formation of unsaturated metal sites in the framework upon the two-stage activation. These results demonstrate that

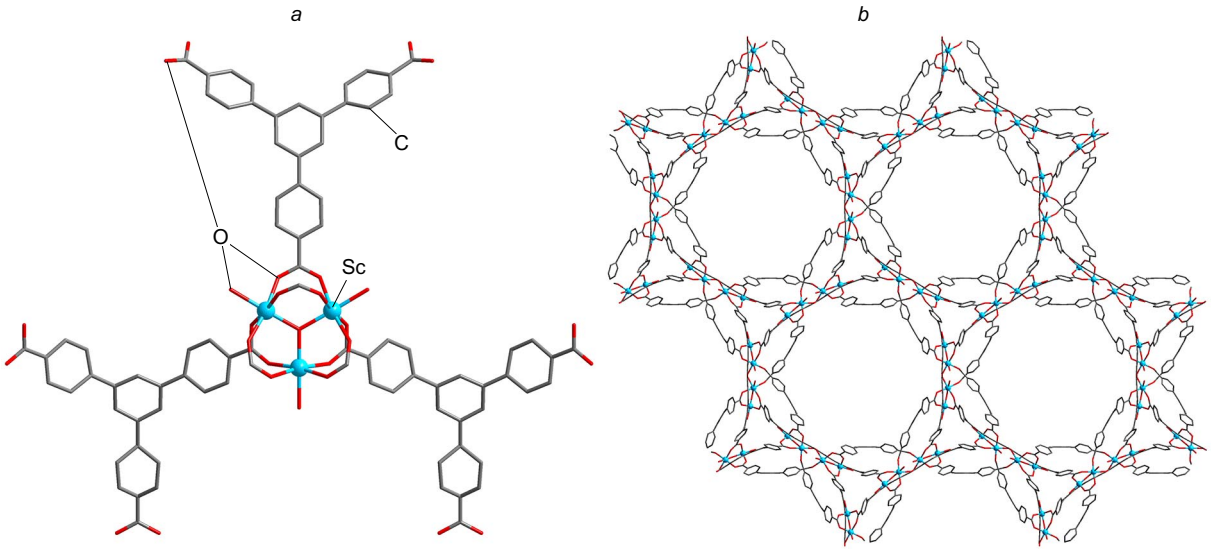


Figure 20. Building block (*a*) and view along the *c* axis (*b*) of the structure of $[Sc_3O(btb)_2(H_2O)_3(OH)]$ (**22**).[53]

appropriate selection of the activation procedure is very important for the manufacture of materials with enhanced gas sorption characteristics.[49]

The compound $[Sc_2(bptc)(OH)_2]\cdot 1.25\,H_2O$ (**23**) (H_4bptc is diphenyl-3,3′,5,5′-tetracarboxylic acid) was obtained by solvothermal synthesis from scandium triflate hydrate and H_4bptc in a slightly acidified DMF–THF–H_2O solvent mixture.[66] The structure of compound **23** is based on the binuclear secondary building block $\{Sc_2(\mu_2\text{-}OH)(RCOO)_4\}$ in which each scandium atom is in the octahedral coordination environment formed by six oxygen atoms, four of which belong to four different $bptc^{4-}$ carboxylate anions and two of which belong to two μ_2-OH groups linking the Sc sites (Fig. 21 *a*). The$\{Sc_2(\mu_2\text{-}OH)(COO)_4\}$ blocks form the $\{Sc_2O_{11}\}$ dioctahedra, which are connected by the bridging $bptc^{4-}$ ligands, thus forming a three-dimensional structure with channels 8.1 Å in diameter (see Fig. 21 *b*).

According to *in situ* powder X-ray diffraction data, compound **23** retains the crystallinity up to 500 °C. Framework **23** can be activated by replacement of the solvent by acetone and subsequent heating. The shape of the N_2 sorption isotherm at 77 K corresponds to type I, which confirms the microporosity of the compound and complete activation of the framework. The pore diameter calculated by the Dubinin–Astakhov method is 7.5 Å, which is generally consistent with structural data. The specific internal surface area S_{BET} is 1350 $m^2\ g^{-1}$. From the H_2 sorption isotherm at 87 K, the total uptake was found to be 2.14 mass % at 1 bar and 3.84 mass % at 20 bar. The heat of adsorption was 5.96 kJ mol^{-1} at zero surface coverage.

Activated compound **23** was tested for sorption of water vapour at room temperature and for the possibility of CO_2 sorption at different relative humidity.[67] It was found that the CO_2 uptake increases from 4.2 mass % under dry conditions to 10.2 mass % at 20% relative humidity at 30 °C. This study was continued by measurement of the selective sorption of CO_2 from a CO_2-CH_4 mixture in the presence of water vapour.[68] The CO_2 uptake of compound **23** was found to be 4.3 mass % at 30 °C; this value increases twofold (9.3 mass %) when the relative humidity increases to 40%.

Ibarra *et al.*[69] also studied the sorption behaviour and selectivity of MOF **23** towards CO_2, N_2 and hydrocarbons (Fig. 22). The compound demonstrated high CO_2 uptakes at low pressure and selectivities for CO_2 adsorption from a CO_2-N_2 mixture comparable with the best known values, with the heat of adsorption being moderate (29.5 kJ mol^{-1}).

The Monte Carlo and DFT calculations show the arrangement of adsorption sites in framework **23** and interpret the high CO_2 uptakes (see Fig. 22 *b*).[69] The interaction of the hydroxy group with the adsorbed CO_2 molecule is additionally stabilized by weak hydrogen bonds between the nearest CH groups. The calculations also explain the high uptake of ethanol (compared with the modest uptakes of non-polar toluene and cyclohexane) by the formation of strong hydrogen bonds between the ethanol molecule and the hydrogen atom of the framework hydroxy group. Meanwhile, in the case of toluene, the arrangement of molecules in the pores of framework **23** is determined by π–π and CH···π interactions between the guest molecules and the aromatic rings of framework walls. The distances between the toluene carbon atoms and the ligand carbon atoms are 3.74 to 4.25 Å.

In a study of iodine vapour sorption by compound **23** and its isostructural analogues $[M_2(bptc)(OH)_2]$ (M = Al, Fe, In), it was found that $[Sc_2(bptc)(OH)_2]$ (**23**) can adsorb up to 1.54 g g^{-1} of iodine, sorption is fully reversible and the framework retains its structure. By combining experimental and theoretical methods, the authors were able to identify the binding sites and the mutual positions of iodine molecules in the framework pores. It was shown that the

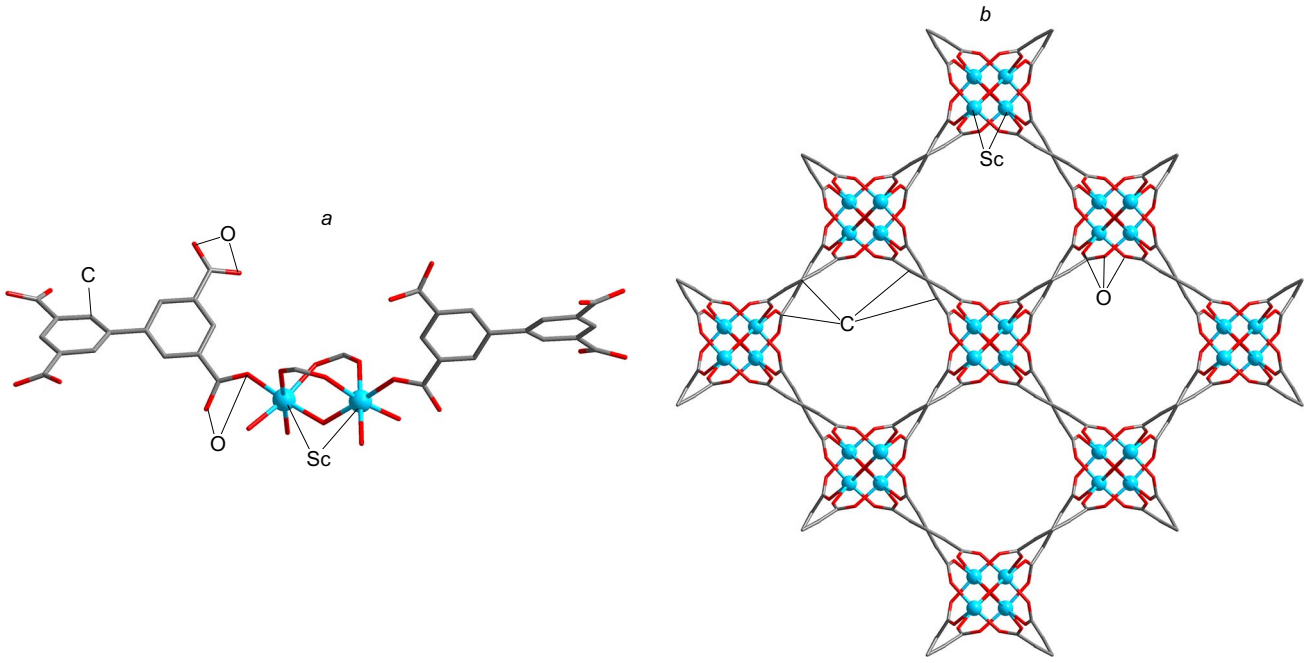


Figure 21. Building block (*a*) and view along the *b* axis (*b*) for the structure of $[Sc_2(bptc)(OH)_2]$ (**23**).[66]

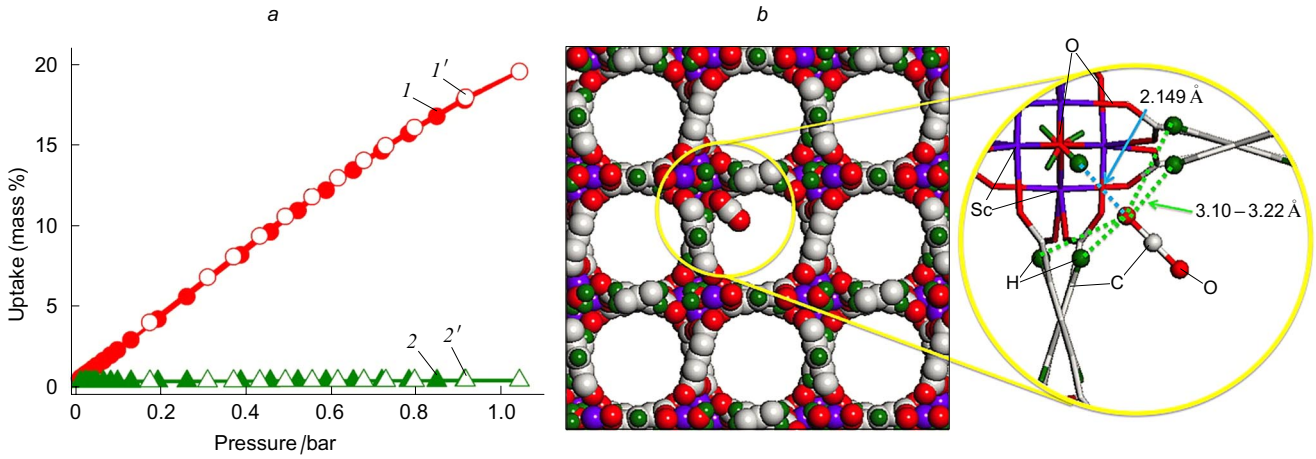


Figure 22. Isotherms of CO_2 (*1*) and N_2 (*2*) sorption and CO_2 (*1′*) and N_2 (*2′*) desorption at 298 K (*a*) and calculated CO_2 adsorption site for $[Sc_2(bptc)(OH)_2]$ (**23**) (*b*).[69] The framework is shown as van der Waals spheres.

iodine molecules are assembled to form chains, which ensures highly efficient sorption by the framework to attain a unique density of guest molecules within the pores (3.08 g cm^{-3}).[70]

The reaction of scandium nitrate with 1,1′-azobenzene-3,3′,5,5′-tetracarboxylic acid (H_4abtc) in DMF led to the synthesis of compound $[Sc_3O(abtc)_{1.5}(H_2O)_3(NO_3)]$ (**24**),[54] which is an analogue of *soc*MOF polymers[99] with scandium as the metal site. The compound structure is based on the trinuclear $\{Sc_3O(RCOO)_6(H_2O)_3\}$ unit (see Fig. 14). These units serve as the lattice points and are connected by diazobenzenetetracarboxylate ligands to form a structure with *soc* topology and pore diameter of 5 Å (Fig. 23). A study of the sorption characteristics of the obtained compound demonstrated that SOF **24** has a larger pore volume measured with respect to nitrogen (0.57 cm^3 g^{-1}) than the isostructural indium analogue $[In_3O(abtc)_{1.5}(H_2O)_3(NO_3)]$ (0.54 cm^3 g^{-1}).[99] Mitchell *et al.*[56] established that compound **24** has a very low efficiency as a catalyst of C–C and C–N bond formation, which may be due to too small pore diameter in the framework, which hampers the access of reactants to the active sites.

A series of eight heterometallic compounds based on doubly and triply charged metal cations (M^{2+} = Mg^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}; M^{3+} = Fe^{3+}, In^{3+}, Ga^{3+}, V^{3+}, Sc^{3+}), structurally similar to compound **24**, were synthesized by the reactions of appropriate metal salts (nitrates, chlorides and acetates) with H_4abtc in solvent mixtures (dimethylacetamide/MeCN – DMF – H_2O) acidified with nitric acid.[71] The sorption properties of the compounds towards CO_2, C_2H_2, CH_4 and H_2 were studied; for $[ScMg_2(abtc)_{1.5}(H_2O)_3(OH)]$; the heat of CO_2 adsorption at zero coverage was determined to be 16.4 kJ mol^{-1}, which is a medium value.

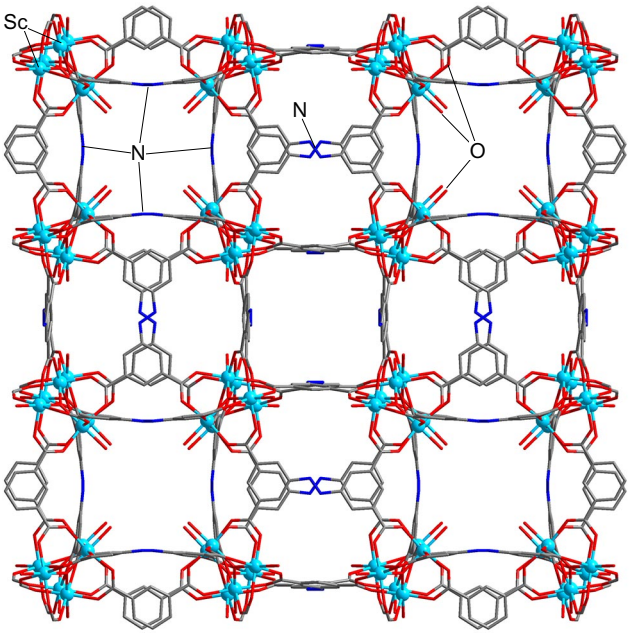


Figure 23. View of structure **24** along the *c* axis.[99]

2.3. Scandium-organic frameworks with heterocyclic carboxylate ligands

The structural chemistry of scandium-based MOFs containing heterocyclic aromatic ligands and either five- or six-membered rings (Fig. 24) is fairly diverse. Heteroatoms present in the ring can not only affect the synthesis and the properties of the obtained compounds, but also be involved in metal coordination giving rise to structures with a new topology. If the Sc^{3+} coordination number increases to 7 or 8, the coordination environment of the cation often includes the nitrogen atom, while Sc^{3+} becomes similar to Y^{3+} in its coordination environment.

The crystals of $[Sc(tdc)(OH)]\cdot 2.6\,H_2O$ (**25**) (H_2tdc is 2,5-thiophenedicarboxylic acid) were prepared by the reaction of scandium triflate hydrate with the appropriate acid in a slightly acidified DMF – THF – H_2O solvent mixture.[66] Like the structure of compound **23**, that of **25** is based on the secondary binuclear building unit, $\{Sc_2(\mu_2\text{-}OH)(COO)_4\}$, in which the scandium atoms are in the octahedral coordination environment and are connected by the tdc^{2-} dicarboxylate ligands, thus forming a three-dimensional structure with channels 6.3 Å in diameter (Fig. 25). According to *in situ* powder X-ray diffraction at elevated temperature, this MOF retains the crystallinity up to 350 °C. Compound

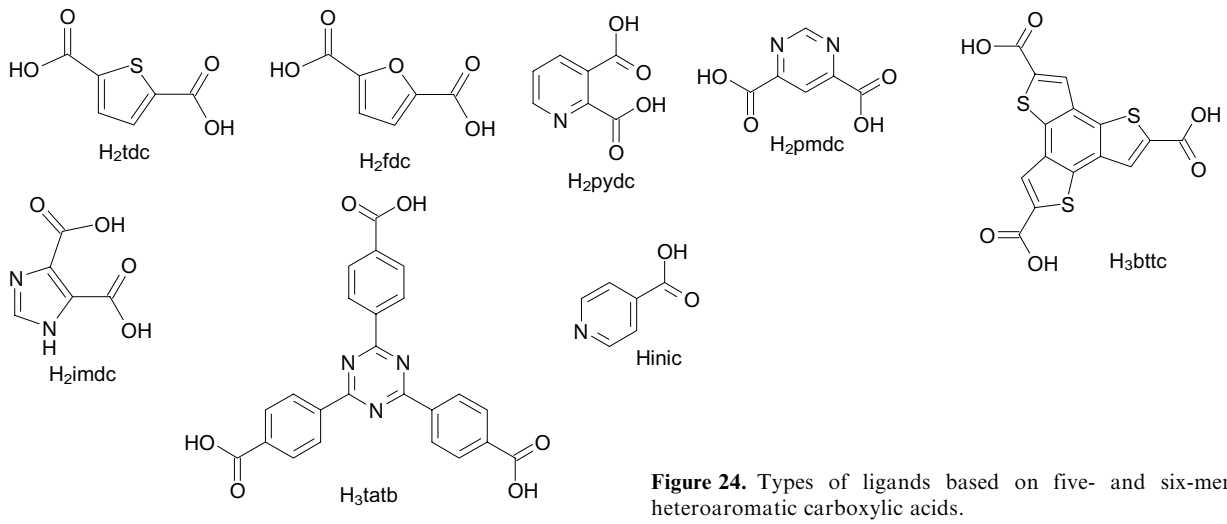


Figure 24. Types of ligands based on five- and six-membered heteroaromatic carboxylic acids.

25 can be activated by replacement of the solvent by acetone followed by heating. The shape of the N_2 sorption isotherm at 77 K corresponds to type I, which confirms the microporosity of the compound and complete activation of the framework. The pore diameter calculated by the Dubinin–Astakhov method is 6.2 Å, which is generally consistent with structural data. The BET specific internal surface area is 1514 $m^2\ g^{-1}$. The H_2 sorption isotherms at 87 K show the total uptake to be 2.31 mass % at 1 bar and 4.44 mass % at 20 bar. The calculated heat of adsorption is 6.65 kJ mol^{-1} at zero surface coverage. In subsequent studies,[69,71] the sorption properties of compound **25** were also investigated.

In a study of the selective sorption of carbon dioxide from a CO_2–CH_4 mixture by compound **25**,[69] the total CO_2 uptake for this compound was 1.47 mass % at 30 °C and zero humidity and seven-fold higher (9.90 mass %) for relative humidity of 40%. In addition, sorption properties and the selectivity of SOF **25** towards CO_2, N_2, alcohols and hydrocarbons were studied; the CO_2 sorption was found to be preferred over nitrogen sorption, while ethanol was found to be preferably sorbed over toluene and cyclohexane.[72] Figure 26 shows the positions of the preferable CO_2 adsorption sites according to the results of Monte Carlo and DFT calculations.[69] In the calculated structure, cooperative interactions were found between the adsorbed CO_2 molecule, hydroxyl group and CH groups. The relatively low uptakes of non-polar toluene and cyclohexane in comparison with ethanol were supported by Monte Carlo calculations. Density functional theory calculations confirmed the formation of strong hydrogen bonds between the ethanol molecule and the framework hydroxyl group.

The reactions of scandium chloride hexahydrate with 2,5-furandicarboxylic acid (H_2fdc) under solvothermal conditions afford frameworks **26**–**28** of various structures depending on the solvent system, temperature and reaction

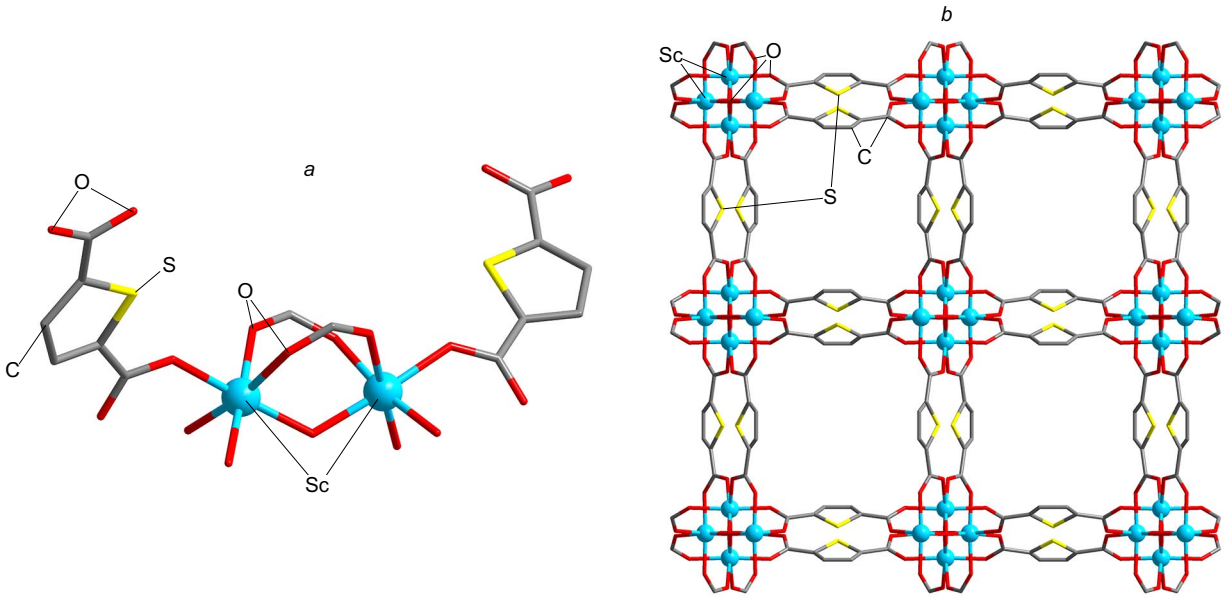


Figure 25. Building block (*a*) and view along the *c* axis (*b*) of the structure of [Sc(tdc)(OH)] (**25**).[66]

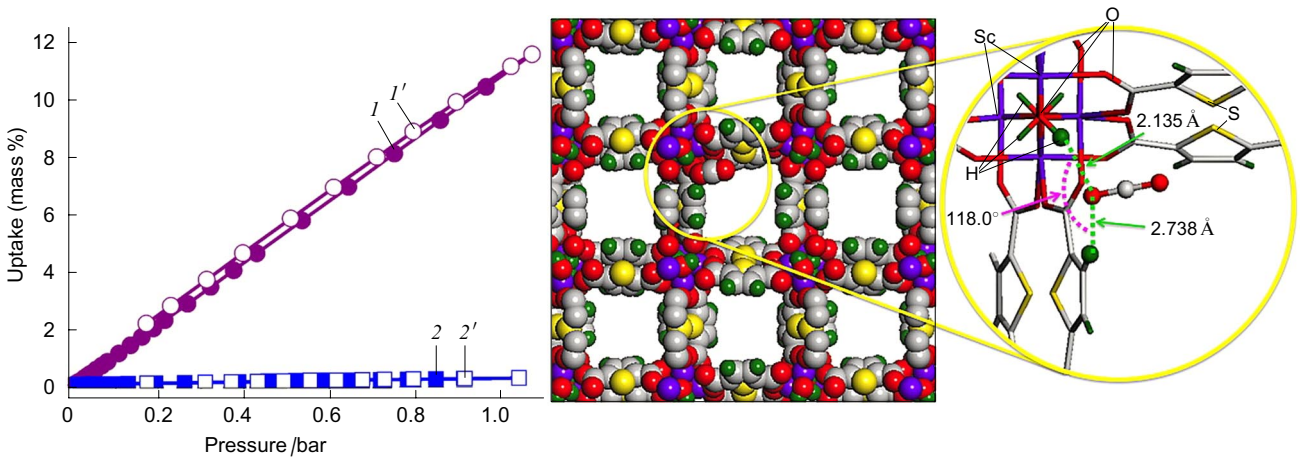


Figure 26. Isotherms of CO_2 (*1*) and N_2 (*2*) adsorption and CO_2 (*1′*) and N_2 (*2′*) desorption at 298 K (*a*) and CO_2 adsorption site for [Sc(tdc)(OH)] (**25**) (*b*).[72] The framework is shown as van der Waals spheres.

time.[73] In the H_2O – DMF – MeCN system (1 : 1 : 6) (80 °C, 24 h), the framework $(Me_2NH_2)[Sc(fdc)_2(H_2O)_2]\cdot 1.5\,MeCN$ (**26**) is formed.[73] According to X-ray diffraction data, the Sc^{III} cations of **26**, which are located in a distorted octahedral environment (Fig. 27 *a*), are joined by bridging furandicarboxylate anions, thus forming layers parallel to the *bc* planes. These layers are joined by hydrogen bonds between the carboxyl groups of the ligand and coordinated water molecules of the neighbouring layers to form a supramolecular framework with one-dimensional pores of 6 × 7 Å size.

The compound $(Me_2NH_2)_2[Sc(fdc)_2(HCOO)]$ (**27**) is formed in a DMF – H_2O (1 : 4) mixture at 120 °C within 7 days. In the structure, the Sc^{III} cations, which are located in a distorted octahedral environment (see Fig. 27 *b*), are connected by two bridging furandicarboxylate anions thus forming chains. The planes of the aromatic rings of the ligands in the chains are parallel and are involved in the π – π stacking interactions. The chains are joined by bridging formate anions to form charged layers. The interlayer space is filled with dimethylammonium cations, which are hydrogen-bonded to the carboxylate groups of the ligands from the layers.

The compound $[Sc_2(fdc)_3(H_2O)_2]$ (**28**) was synthesized under hydrothermal conditions at 120 °C within 24 h. In the structure of **28**, two crystallographically independent scandium cations are connected by bridging carboxylate anions (see Fig. 27 *c*), thus forming layers. The layers are, in turn, connected *via* hydrogen bonds between the coordinated water molecules and the ligand carboxylate groups.

It was shown that SOF **28** is thermally stable (up to 320 °C) and exceptionally stable in the pH range from 1 to 13, with the structure being retained for at least two weeks in acidic or alkaline medium.

The coordination polymer $[Sc(inic)_2(OH)(H_2O)]$ (**29**) (Hinic is isonicotinic acid) was obtained by the reaction of scandium nitrate with isonicotinic acid under hydrothermal conditions.[74] Structure **29** has two types of scandium cations. The Sc(1) cations are in an octahedral coordination environment composed of six oxygen atoms, two from crystallographically independent isonicotinate anions, two from hydroxide anions and two from coordinated terminal water molecules. The Sc(2) cations are in the octahedral coordination environment composed of four oxygen atoms of four independent isonicotinate anions and two oxygen atoms of two hydroxide anions (Fig. 28 *a*). One of the

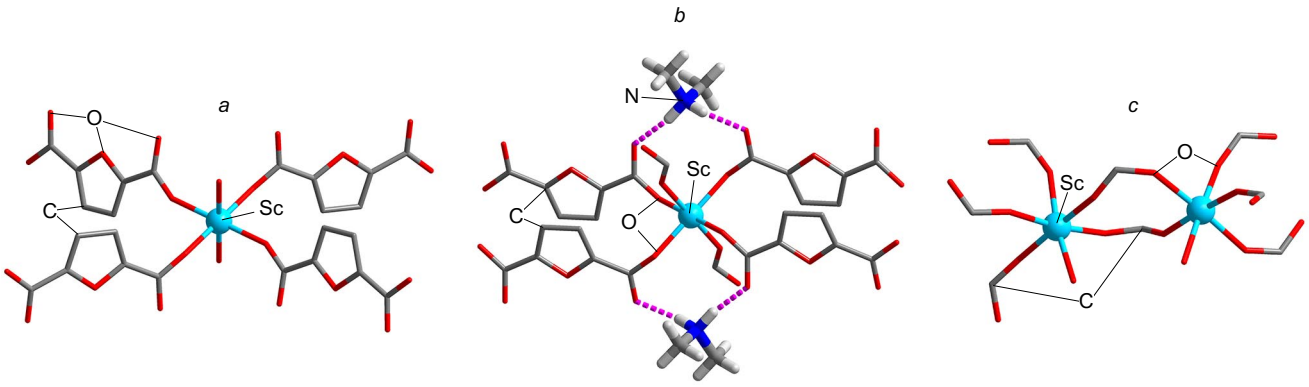


Figure 27. Coordination environment of scandium atoms in the structures of $(Me_2NH_2)[Sc(fdc)_2(H_2O)_2]\cdot 1.5\,MeCN$ (**26**) (*a*), $(Me_2NH_2)_2[Sc(fdc)_2(HCOO)]$ (**27**) (*b*), $[Sc_2(fdc)_3(H_2O)_2]$ (**28**) (*c*).[73]

isonicotinate anions and one of the hydroxide anions act as bridges and connect the Sc(1) and Sc(2) cations in pairs, thus forming chains along the *a* axis. The neighbouring chains are joined *via* π – π stacking interactions between the pyridine rings of the ligands (the distance between the ring planes is 3.3 Å) (see Fig. 28 *b*).

The compound $\{Sc_3(imdc)_4(H_2O)_4](NO_3)\ H_2O\}$ (**30**) obtained by the reaction of scandium nitrate with imidazole-4,5-dicarboxylic acid (H_2imdc) on heating in acetonitrile acidified with hydrochloric acid also contains two types of scandium cations.[74] The Sc(1) cations occur in a coordination environment composed of four oxygen atoms and four nitrogen atoms from four independent imidazoledicarboxylate anions chelating the metal cation. The Sc(2) cations are situated in an octahedral coordination environment composed of four oxygen atoms of carboxylate groups of two independent ligands and two oxygen atoms of two hydroxide anions. The Sc(1) and Sc(2) cations are connected by bridging imidazoledicarboxylate, thus forming chains along the *c* axis. The chains are composed of butterfly-shaped moieties and are not connected to neighbouring chains (Fig. 29).

Investigation of catalytic activity of compounds **29** and **30** towards cyanosilylation of aromatic aldehydes showed that both compounds are selective heterogeneous catalysts; the use of compound **29** provides quantitative yields in the case of substituted benzaldehydes and a yield of 74% in the case of naphthalene-1-carbaldehyde. Compound **30** is less active, the product yields being 30% to 50% in all cases except for the nitro-substituted benzaldehyde (98%).

A series of three SOFs of different dimensionality based on common binuclear units was obtained.[75] All three com-

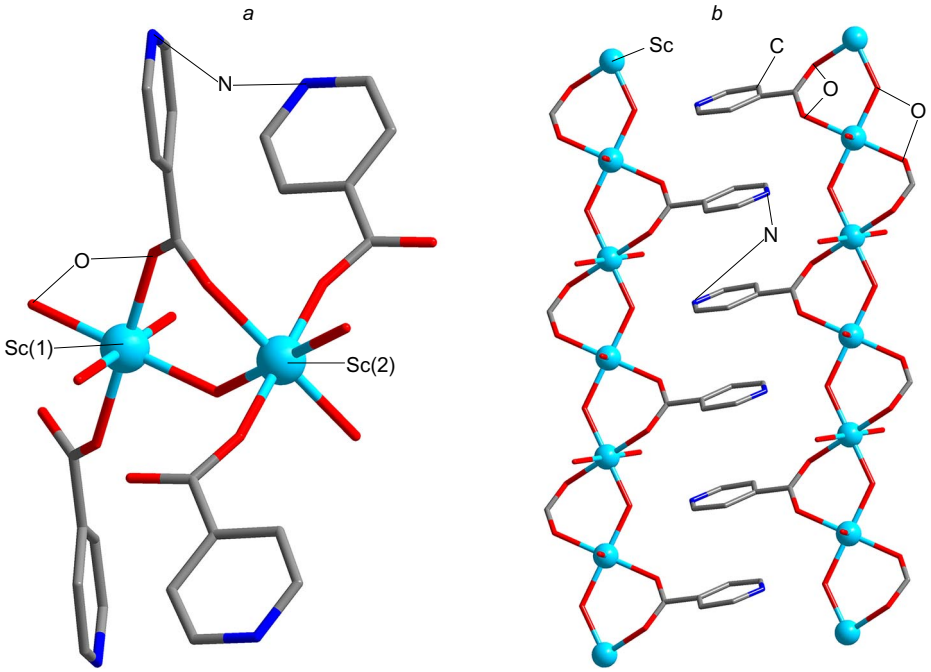


Figure 28. Building block (*a*) and view along the *b* axis (*b*) of the structure of $[Sc(inic)_2(OH)(H_2O)]$ (**29**).[74]

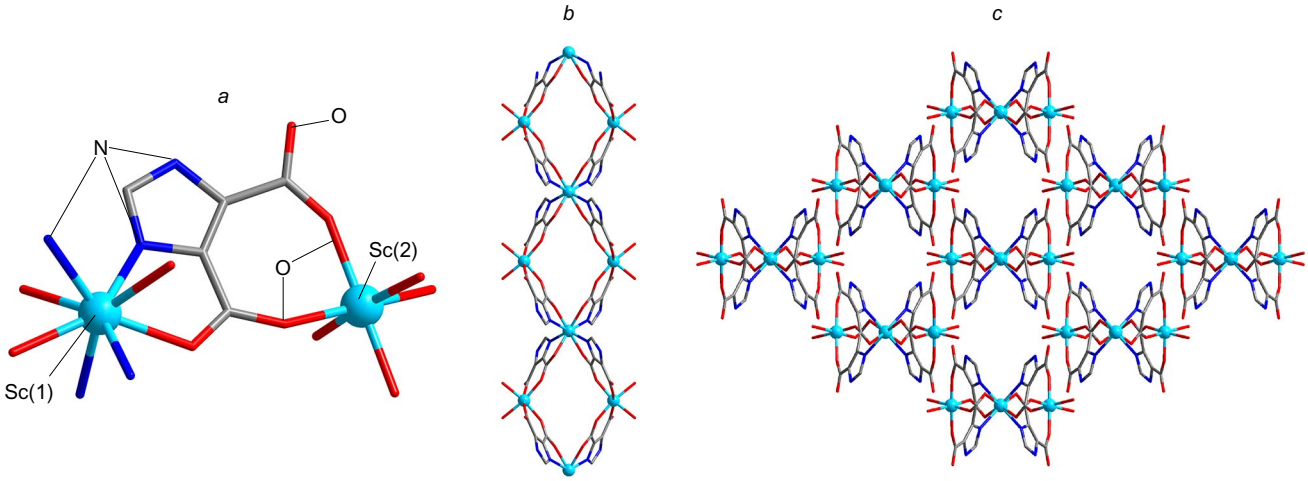


Figure 29. Building block (*a*) and view along the *b* (*b*) and *c* (*c*) axes of the structure of $[Sc_3(imdc)_4(H_2O)_4](NO_3)\cdot H_2O$ (**30**).[74]

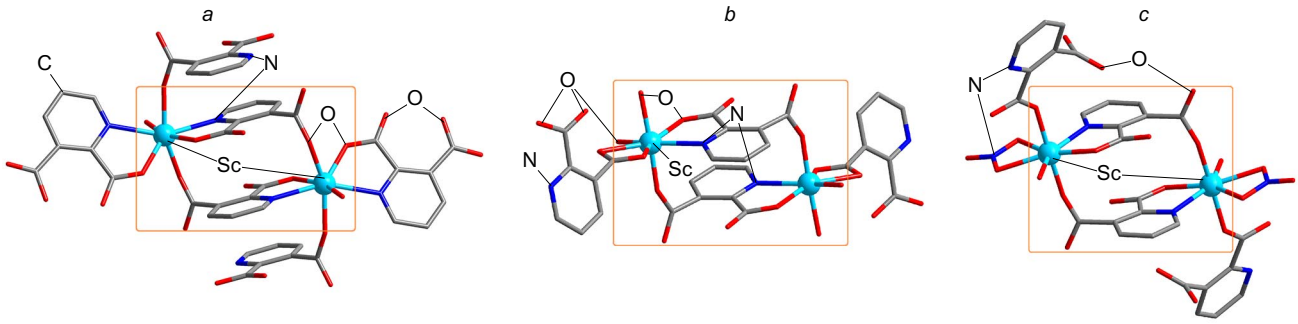


Figure 30. Structure of the binuclear moiety $\{Sc_2(pydc)_2\}$ in compounds **31** (*a*), **32** (*b*) and **33** (*c*).[75]

pounds have a similar structural motif — $\{Sc_2(pydc)_2\}$ (H_2pydc is pyridine-2,3-dicarboxylic acid) — differing in the pattern of connections of the ligand to the units; in the authors' opinion, this is a consequence of $pydc^{2-}$ binding specifics and similar conditions of synthesis.

The chain-like compound $\{[Sc(pydc)(Hpydc)(H_2O)]\cdot H_2O\}$ (**31**) was prepared by the reaction of scandium chloride hexahydrate with pyridine-2,3-dicarboxylic acid in water in an alkaline medium (pH 12.5).[75] The scandium atoms in this structure are in a coordination environment with C.N. = 7 consisting of five oxygen atoms, four of which belong to the carboxyl groups of the ligand, while the fifth atom belongs to a coordinated water molecule, and two nitrogen atoms of the ligand pyridine ring (Fig. 30 *a*). The $pydc^{2-}$ ligands are bridging and are coordinated to two scandium cations thus forming the $\{Sc_2(pydc)_2\}$ building blocks, which are connected along the *a* axis to form ladder-shaped chains. The additional terminal chelating ligands $pydc^{2-}$ are coordinated to each chain. The chains are connected to one another *via* hydrogen bonds with the water molecules of crystallization and form, in this way, a three-dimensional structure (Fig. 31).[75]

The layered compound $\{[Sc_2(pydc)_3(H_2O)_4]\ 5\,H_2O\}$ (**32**) was synthesized under analogous conditions, but at higher pH (12.8) and over a longer reaction time (2 days).[75] According to X-ray diffraction data, two types of crystallographically independent scandium atoms, Sc(1) and Sc(2), are present in the structure. The coordination polyhedron of Sc(1) can be conceived as a distorted pentagonal bipyramid, with the equatorial plane being formed by two nitrogen atoms and two oxygen atoms of two $pydc^{2-}$ ligands and the oxygen atom of the coordinated water molecule. The axial positions are occupied by the oxygen atoms of the carboxylate group and coordinated water molecule (see Fig. 30 *b*). The Sc(2) atom is located at the centre of a distorted pentagonal bipyramid and has a coordination environment composed of six oxygen atoms and one nitrogen atom. The Sc(1) atoms are connected into chains, which, in turn, form layers in the *ab* plane by being linked to the Sc(2) sites *via* the pyridinedicarboxylate bridging ligands. The layers form a supramolecular three-dimensional structure *via* hydrogen bonds formed between them (Fig. 32).

The framework $[Sc(pydc)(H_2O)(NO_3)]$ (**33**) is formed in the reaction of scandium nitrate hexahydrate with pyridine-2,3-dicarboxylic acid in water under hydrothermal condi-

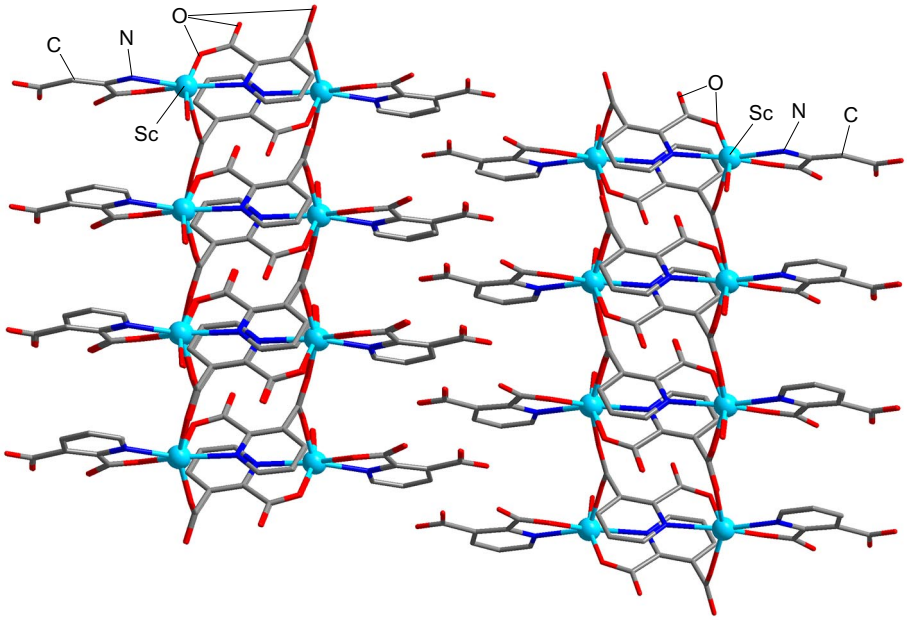


Figure 31. Structure of the ladder polymer $\{[Sc(pydc)(Hpydc)(H_2O)]\cdot H_2O\}$ (**31**), view along the [100] axis.[75]

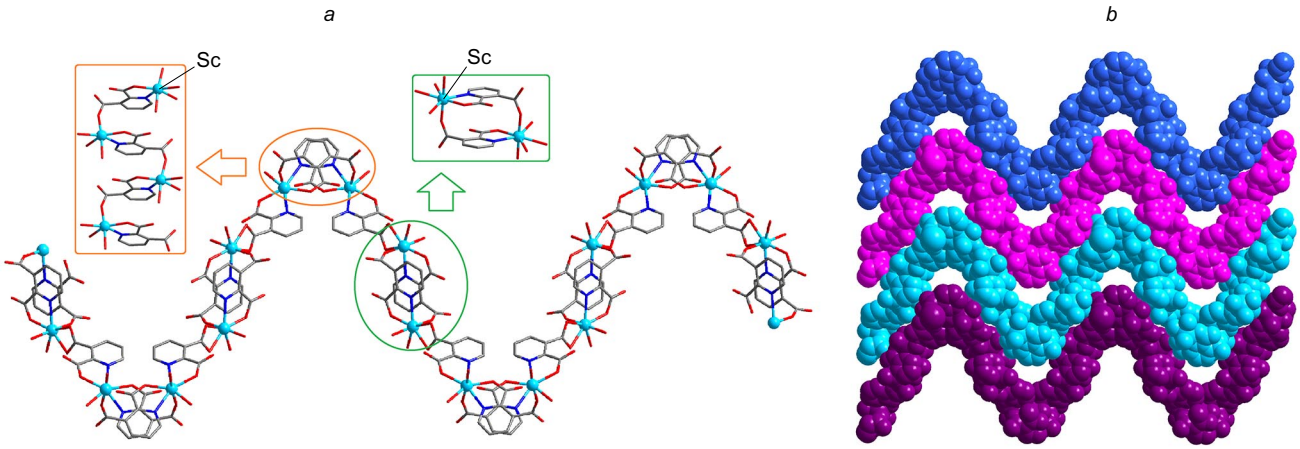


Figure 32. Layer (*a*) and view along the [100] axis (*b*) of the structure of $[Sc_2(pydc)_3(H_2O)_4]\cdot 5\,H_2O$ (**32**).[75]

tions (100 °C, 24 h) without alkali.[75] According to X-ray diffraction data, there is one crystallographically independent scandium atom in the structure. The coordination polyhedron can be conceived as a distorted pentagonal bipyramid, with the vertices being occupied by three carboxyl oxygen atoms of three different $pydc^{2-}$ ligands, one pyridine nitrogen atom of the ligand, two oxygen atoms of the nitrate anions and one oxygen atom of the terminal water molecule (see Fig. 30 *c*). A pair of $pydc^{2-}$ ligands symmetrically bind two scandium atoms to form the $\{Sc_2(pydc)_2\}$ unit structurally similar to the secondary building blocks of compounds **31** and **32**. These units are joined by the bridging $pydc^{2-}$ ligands to form helices along the *c* axis. It is of interest that two types of helices, left- and right-handed ones, are present in the structure (Fig. 33). Each left-handed helix is connected to three neighbouring right-handed helices through the $\{Sc_2(pydc)_2\}$ secondary building block, while each right-handed helix is connected to three neighbouring left-handed helices. The left-handed and right-handed helices form a three-dimensional structure with the niobium(II) oxide topology **nbo-a**.

Compounds **31** – **33** show rather high hydrolytic (when kept in water for 5 days) and thermal (up to 350 °C) stability. In a catalytic activity study, MOFs **31** – **33** behaved as efficient heterogeneous catalysts in the cyanosilylation of *p*-nitrobenzaldehyde (> 85% conversion).[75]

Scandium-organic frameworks with pyrimidine-4,6-dicarboxylic acid are also structurally diverse.[35] Variation of the conditions of synthesis gave rise to three coordination polymers with different structure: $\{[Sc(pmdc)(ox)_{0.5}(H_2O)_2]\cdot 3\,H_2O$ (**34**, pmdc is pyrimidine-4,6-dicarboxylate, ox is oxalate), $[Sc(pmdc)(OH)(H_2O)]\cdot H_2O$ (**35**) and $[Sc_2(pmdc)(OH)_3Cl]\cdot DMF\cdot 2\,H_2O$ (**36**)$\}$. According to X-ray diffraction data, the scandium atom in compound **34** is chelated by two $pmdc^{2-}$ ligands and an oxalate anion (formed upon partial decomposition of $pmdc^{2-}$) and is also coordinated by two water molecules. The coordination polyhedron is a trigonal dodecahedron. The scandium atoms are connected by bridging $pmdc^{2-}$ ligands to form chains along the *b* axis. The chains are connected by bridging oxalate anions, thus forming hexagonal channels along the *c* axis (Fig. 34). Compound **34** is composed of neutral layers of the honeycomb topology (**hcb**) with water

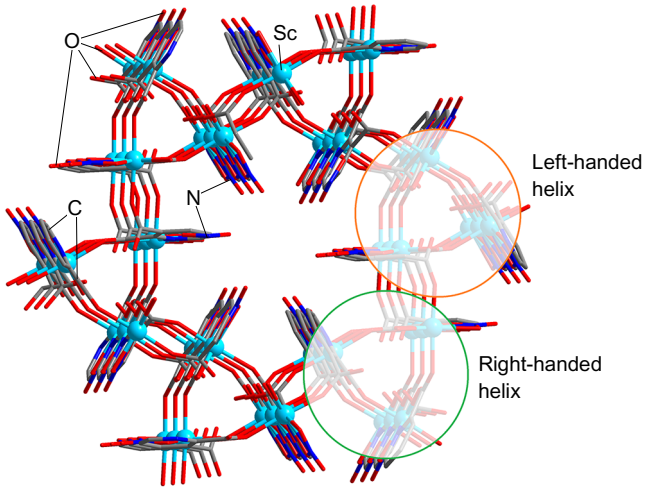


Figure 33. View of the structure of $[Sc(pydc)(H_2O)(NO_3)]$ (**33**) along the [110] axis.[75]

molecules crystallized between them and is isostructural to the previously described lanthanide-based coordination polymers.[100]

According to X-ray diffraction data, the scandium atom in **35** is coordinated by two chelating $pmdc^{2-}$ ligands, one terminal water molecule and two bridging hydroxide anions. The resulting coordination polyhedron is a highly distorted pentagonal bipyramid. The bridging hydroxide anions link two scandium cation, thus forming the $[Sc_2(pmdc)_4(OH)_2(H_2O)_2]^{4-}$ dimer (Fig. 35). These dimers are connected by bridging $pmdc^{2-}$ ligands to give layers with **sql** topology, which are hydrogen-bonded to one another.

The composition of compound **36**, $\{[Sc_2(pmdc)(OH)_3Cl]\ DMF\cdot 2\,H_2O\}$, was established by elemental analysis and energy dispersive X-ray spectroscopy. The presence of the ligand was confirmed by IR spectroscopy and solid-state ^{13}C NMR spectroscopy, while unit cell parameters were determined by powder X-ray diffraction. The authors also investigated sorption characteristics of compound **36** activated in different ways. Direct activation by heating did not completely eliminate the guest

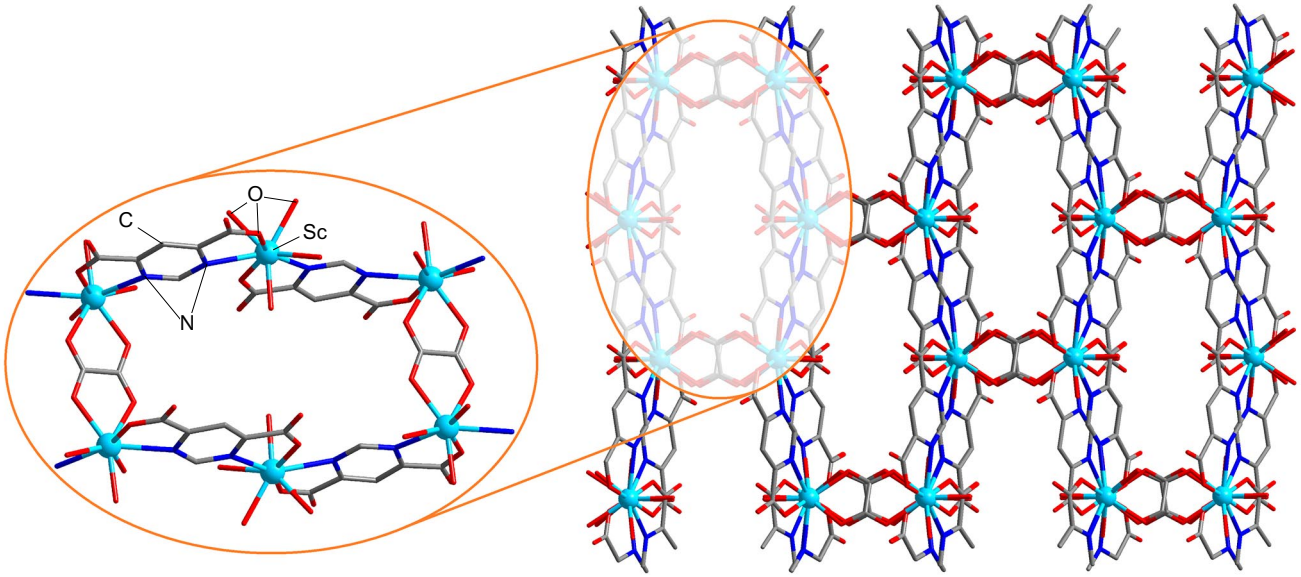


Figure 34. View of the structure of $[Sc(pmdc)(ox)_{0.5}(H_2O)_2]\cdot 3\,H_2O$ (**34**) along the *c* axis.[35]

molecules from the framework, as indicated by low gas uptakes at low temperature. Therefore, the compound was additionally preactivated by replacing the guest molecules with more volatile methanol and then heated. The sample additionally kept in methanol had an almost twice higher gas sorption capacity, as evidenced by the nitrogen sorption isotherm at the same temperature. The shape of CO_2 sorption isotherms corresponds to type I characteristic of microporous compounds and the heat of adsorption is 28 kJ mol^{-1}.

Cepeda *et al.*[76] obtained the heterometallic compounds $[ScLi(pmdc)_2(H_2O)]$ (**37**) and $[ScNa(pmdc)_2(H_2O)]$ (**38**). It was shown that the type of additional cation, the crystallinity, sorption properties and ionic conductivity depend on the conditions of synthesis. The compounds were isostructural with the known compounds $[CdM(pmdc)_2(H_2O)_2]$ (M = Cd, Mn, Zn).[101] Two types of units were present in the structures of both compounds (Fig. 36). The first one are scandium cations located in a coordination environment of four oxygen atoms of the ligand carboxyl groups and four nitrogen atoms of the pyrimidine rings belonging to four chelating ligands. Units of the second type are alkali metal cations located in a distorted octahedral environment consisting of four carboxylate oxygen atoms of the non-chelating ligand and two water molecules. The units are connected to one another, thus forming a three-dimensional structure with the **nbo** topology. The structure has several types of cavities differing in the size: cubic cavities of 9.4 Å size and smaller cavities of ~6 Å size (see Fig. 36).

The sorption properties of compounds **37** and **38** were calculated by the Monte Carlo method and later confirmed experimentally. The ionic conductivity was measured for Mn^{2+}- and Cd^{2+}-doped samples. According to solid-state NMR data, the scandium cations in the doped samples are partly replaced by manganese and cadmium cations, which leads to a greater number of lithium cations in **37** for charge balancing and to approximately an order of magnitude higher lithium conductivity. Keeping of the initial frameworks in solutions of $LiBF_4$ or $NaPF_6$ had a more pronounced effect and increased the ionic conductivity to 4.2×10^{-4} and 9.2×10^{-5} S cm^{-1} for $[ScLi(pmdc)_2(H_2O)]$ and $[ScNa(pmdc)_2(H_2O)]$, respectively.

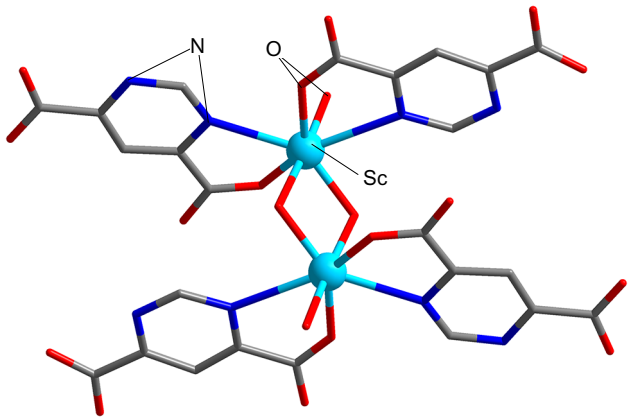


Figure 35. Building block of $[Sc(pmdc)(OH)(H_2O)]\cdot H_2O$ (**35**).[35]

Feng and co-workers[77,78] reported the synthesis of two series of isoreticular coordination polymers with ultra-large pores — PCN-332 (**39**) and PCN-333 (**40**) with the compositions $[Sc_3O(bttc)_2(H_2O)_3(OH)]$ and $[Sc_3O(tatb)_2(H_2O)_3(OH)]$, respectively, which were structurally similar to MIL-100 and framework **21**. Compounds **39** and **40** were prepared by the reactions of scandium chloride and the appropriate acid (H_3bttc is benzo-trithiophenetricarboxylic acid for PCN-332 and H_3tatb is 4,4′,4″-*s*-triazine-2,4,6-triyltribenzoic acid for PCN-333) under solvothermal conditions. The functionalization of compound **40** by post-synthetic modification and the luminescent properties of the product thus obtained were studied.[78] Using the method developed by the authors, some of the linkers in the initial framework were replaced by 1,3,5-benzenetribenzoic acid with an accessible hydroxy or amino group in the central ring, and in the next stage, various substituents (*e.g.*, a substituent containing a terminal azido

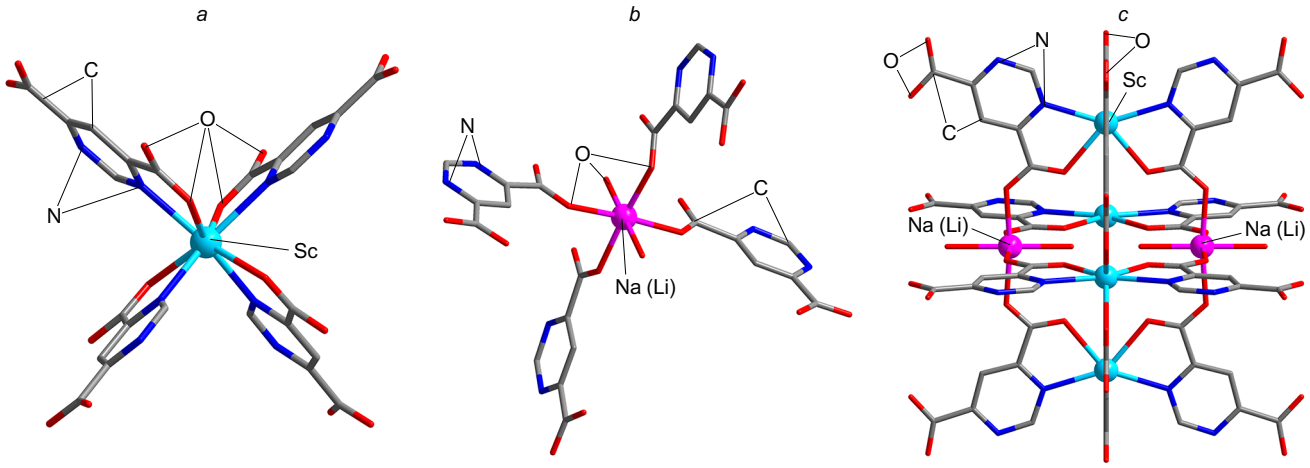


Figure 36. Coordination environment of scandium (*a*) and alkali metal (Na, Li) (*b*) ions in $[ScLi(pmdc)_2(H_2O)]$ (**37**) and $[ScNa(pmdc)_2(H_2O)]$ (**38**); connection of building blocks (*c*).[76]

group) were introduced to this group. The BODIPY ligand known for its fluorophore properties was introduced *via* a click reaction into the resulting framework bearing the azido group and, hence, the framework acquired luminescent properties.

3. Structure and properties of scandium-organic frameworks based on sulfonate ligands

Sulfonate derivatives are also suitable as ligands for the synthesis of SOFs (Fig. 37). These compounds differ from carboxylate ligands by the presence of the third oxygen atom, which can be either coordinated to the central cation or uncoordinated. Scandium-organic frameworks are synthesized using various benzene- and naphthalenesulfonic acids.

Perles *et al.*[79] obtained the compounds $[Sc_2(1,5\text{-nds})(OH)_4]$ (**41**) and $[Sc_2(2,6\text{-nds})(OH)_4]$ (**42**). The synthesis was carried out under hydrothermal conditions by the reaction of scandium(III) chloride with disulfonic acid. The two compounds are structurally similar (Fig. 38 *a*,*b*). The scandium cation occurs in an octahedral coordination environment composed of six oxygen atoms, two belonging to the bridging sulfonic groups and the other four belonging

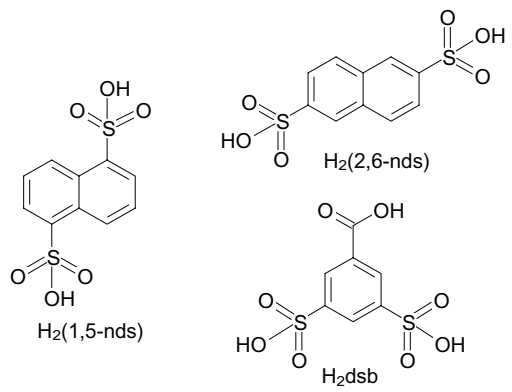


Figure 37. Types of sulfonate ligands based on arenesulfonic acids.

to hydroxide anions. The hydroxide anions function as bridging ligands connecting the scandium cations into zigzag-like chains along the *a* axis (compound **41**) (Fig. 38 *c*) or along the [110] direction (compound **42**) (Fig. 38 *d*). The chains are linked by bridging O–S–O groups in the *ab* plane and by bridging 1,5-nds and 2,6-nds ligands, respectively, along the *c* axis.

The catalytic activity of compounds **41** and **42** was studied for epoxidation of linalool and oxidation of methyl phenyl sulfide with hydrogen peroxide. Both compounds proved to be selective heterogeneous catalysts for the reaction with linalool (60% and 100%, respectively). In the oxidation of methyl phenyl sulfide, both frameworks provided 100% conversion and showed higher efficiency than scandium succinate and terephthalate.[40,41,44]

The hydrothermal reaction of scandium nitrate hexahydrate with 3,5-disulfobenzoic acid (H_2dsb) affords compounds **43**–**46** differing in the composition and structure, depending on the reaction conditions (pH, temperature and time).[80] Thus the compound $[Sc_3(dsb)_2(O_2H_3)(OH)_2(H_2O)_2]$ (**43**, O_2H_3 is the symmetrical aqua hydroxide anion) is formed when the reaction mixture is kept in an autoclave at 200 °C and pH 3.5 for 24 h. When pH is reduced to 2.8, the reaction at 220 °C in the presence of Na_2dsb affords $[Sc_3(dsb)_2(OH)_3(H_2O)_4]$ (**44**). The increase in the pH to 4, with the reaction time being 15 h, promotes the formation of $[Sc_3(dsb)(OH)_6(H_2O)]$ (**45**). In the presence of Na_2dsb and phenanthroline at pH 3.5 and a temperature of 170 °C, the product $[Sc(dsb)(phen)(H_2O)](H_2O)$ (**46**) is formed in 8 days.

According to X-ray diffraction data, the structure of compound **43** contains the $\{(ScO_6)-(O_2H_3)-(ScO_6)\}$ units as secondary building blocks (Fig. 39 *a*). These secondary building blocks are connected along the *b* and *c* axes by the bridging carboxylate and sulfone groups. The layers are linked by hydrogen bonds between the coordinated water molecules and the sulfonate oxygen atoms, thus giving rise to a three-dimensional structure with the fluorite CaF_2 topology.

The structure of **44** comprises two crystallographically independent scandium cations in a coordination environment of six oxygen atoms (Fig. 39 *b*). The secondary build-

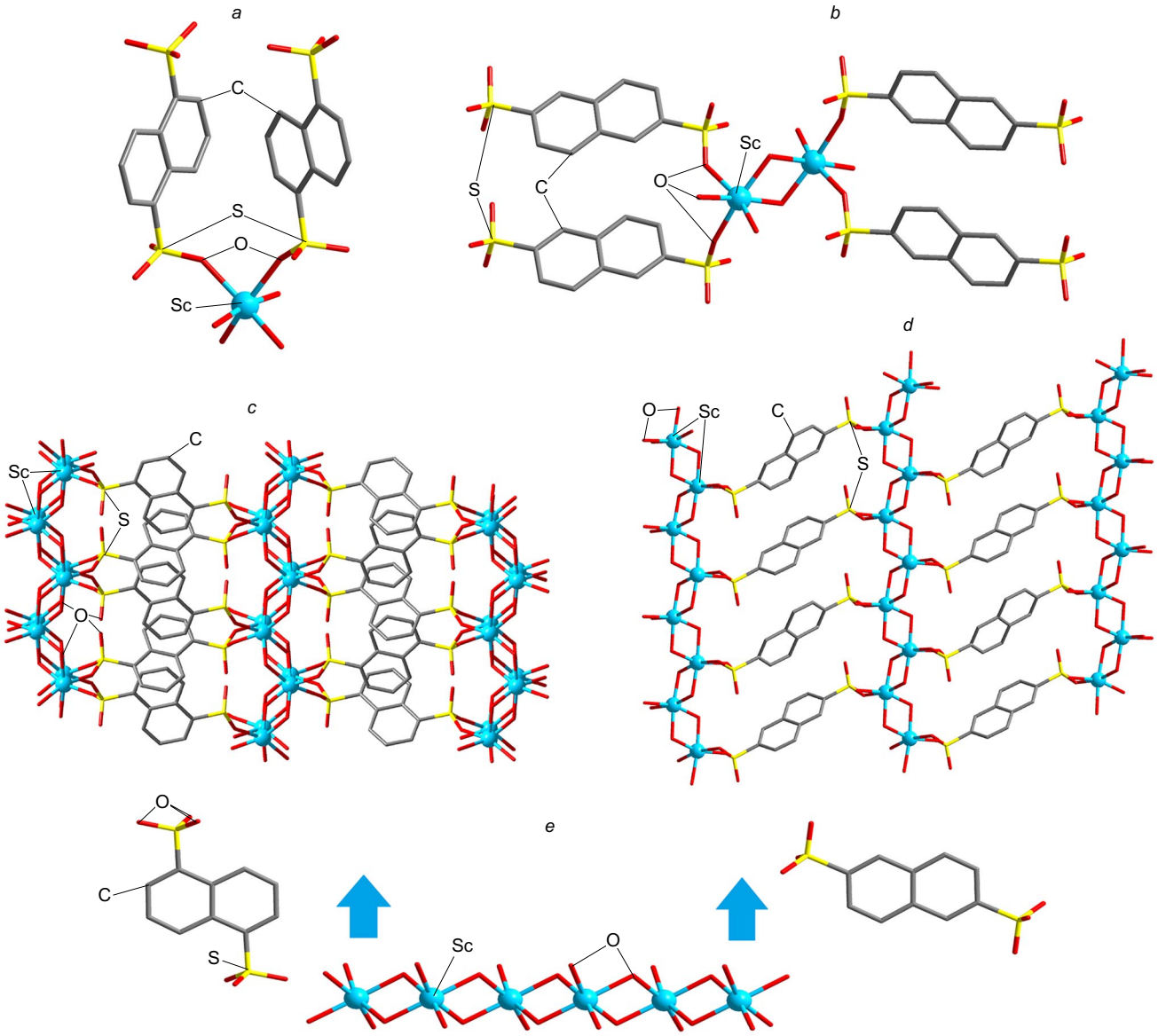


Figure 38. Building blocks of compounds $[Sc_2(1,5\text{-nds})(OH)_4]$ (**41**) (*a*), $[Sc_2(2,6\text{-nds})(OH)_4]$ (**42**) (*b*) and construction pattern (*e*) of frameworks **41** (*c*) and **42** (*d*).[79]

ing blocks in this compound consist of infinite chains of the $\{ScO_6\}$ moieties connected by the bridging hydroxide and carboxylate anions. The chains are connected along the [010] direction through bridging sulfone groups, thus forming a layered structure with the **sql** topology. Like in the above case, the layers are linked by hydrogen bonds to give a three-dimensional structure with **pcu** topology.

According to X-ray diffraction data, the structure of compound **45** contains three crystallographically independent scandium cations situated in an octahedral coordination environment of six oxygen atoms (Fig. 39 *c*). The octahedra are joined by sharing vertices to form trinuclear secondary building blocks $\{Sc_3(\mu\text{-}OH)_3\}^{6+}$, each of them sharing a face with another one; this gives rise to hexanuclear metal centres connected into an inorganic layer of nine-membered rings parallel to the (110) plane. The layers are linked *via* bridging ligands along the [100] direction, thus forming a three-dimensional structure with the **hcb** hexagonal topology.

In compound **46**, the scandium cation is in a coordination environment of four oxygen atoms of the carboxyl groups, one oxygen atom of the coordinated water molecule and two nitrogen atoms of the ligand (Fig. 39 *d*). The ligand binds simultaneously three scandium cations, thus forming a corrugated structure along the [001] axis. These chains are joined by hydrogen bonds along the [010] direction and form layers parallel to the (011) plane. Between the layers, $\pi-\pi$-stacking interactions arise and hydrogen bonds are formed.

The authors thoroughly investigated the catalytic properties and equilibrium transitions between structures **44** and **43** upon replacement of the bridging hydroxyl group by the aqua hydroxo group. The catalytic activity of compounds was studied for the cyanosilylation reaction. The reaction kinetics was found to depend on the substrate nature and

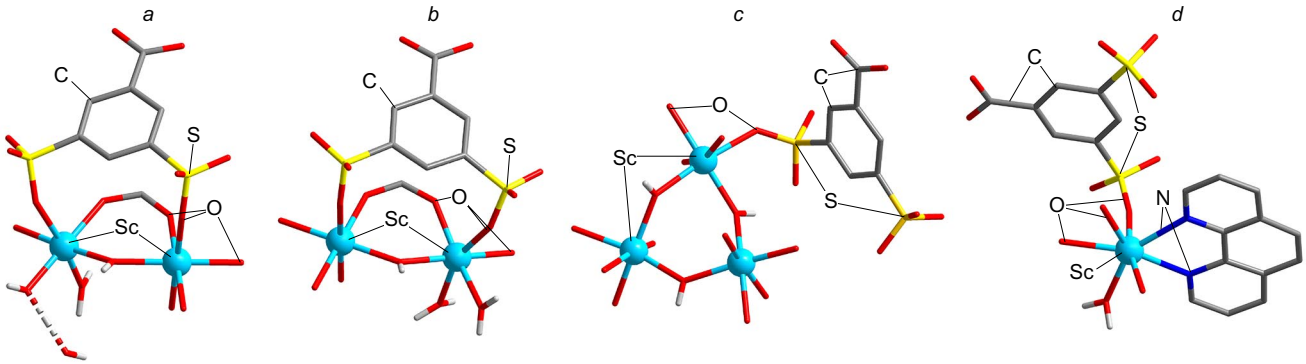


Figure 39. Building blocks of compounds **43** (*a*), **44** (*b*), **45** (*c*) and **46** (*d*).[80]

the number of acidic active sites, which are formed upon elimination of the labile water molecule under the action of aldehyde. Catalytically active sites can polarize carbonyl groups and thus facilitate the nucleophilic addition.

Stabilization of such compounds as stable MOFs opens up the opportunities to study the proton conductivity, water decomposition reactions and enzymatic hydrogen transfer reactions.

4. Structure of scandium-organic frameworks based on N-oxide ligands

N-Oxide ligands are somewhat distinct from other oxygen-containing linkers. Since there is only one oxygen atom capable of coordination to the central atom, the frameworks become more flexible and adaptive, which often leads to interpenetration of the frameworks. Furthermore, the monodentate nature of N-oxide ligands does not favour the assembly of polynuclear secondary building blocks around the donor oxygen atom; all such scandium-organic frameworks are based on inorganic units containing a single Sc^{III} cation.

The compounds $[Sc(bpyO)_3(NO_3)_3]$ (**47**) and $\{[Sc(bpyO)_3](CF_3SO_3)_3(MeOH)_{2.7}(H_2O)_3\}$ (**48**) were prepared by the reaction of scandium nitrate hydrate and scandium triflate with 4,4′-bipyridine *N*,*N*′-dioxide (bpyO) hydrate in methanol and in a methanol–dichloromethane mixture, respectively.[81] The products $[Sc(bpyO)_3](ClO_4)_3$ (**49**) and $[Sc(bpyO)_4(H_2O)_2](ClO_4)_3$ (**50**) were obtained under hydrothermal conditions by the reaction of scandium perchlorate with the ligand in various ratios. According to X-ray diffraction data, compounds **47** – **49** are composed of octahedral blocks $\{ScO_6\}$, which are linked by linear bpyO bridges. Compound **47** contains two interpenetrating rhombohedral frameworks related by a C_2 symmetry axis ($4^{12}6^3$ topology), while the remaining free space in the structure is occupied by nitrate anions. The structure of **49** is very similar to the structure of compound **47** and represents two interpenetrating frameworks; however, as distinct from MOF **47**, the cavities are filled with the guest perchlorate anions and have a somewhat larger volume.

In compound **48**, the scandium cation is situated in a distorted octahedral environment of six oxygen atoms and six bridging ligands. The channels along the *a* and *b* axes present in this structure are filled with triflate anions and guest methanol and water molecules. The topology of MOF **48** differs from that of **47** and is described as 4^86^68 (Fig. 40).

The framework in compound **50** has a noticeably different topology, although it is also composed of six-connected units. Each scandium cation is coordinated by four bridging bpyO ligands and two bridging water molecules. Considering only the bpyO bridges, the Sc^{III} cations appear to be

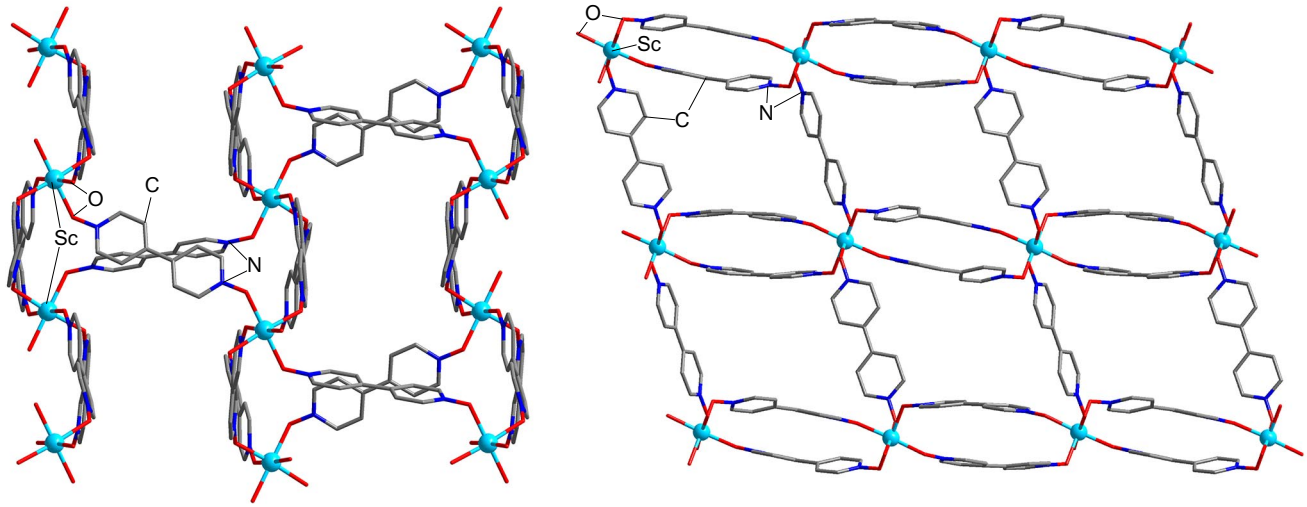


Figure 40. View of the structure of $\{[Sc(bpyO)_3](CF_3SO_3)_3(MeOH)_{2.7}(H_2O)_3\}$ (**48**) along the *a* (on the left) and *b* (on the right) axes.[81]

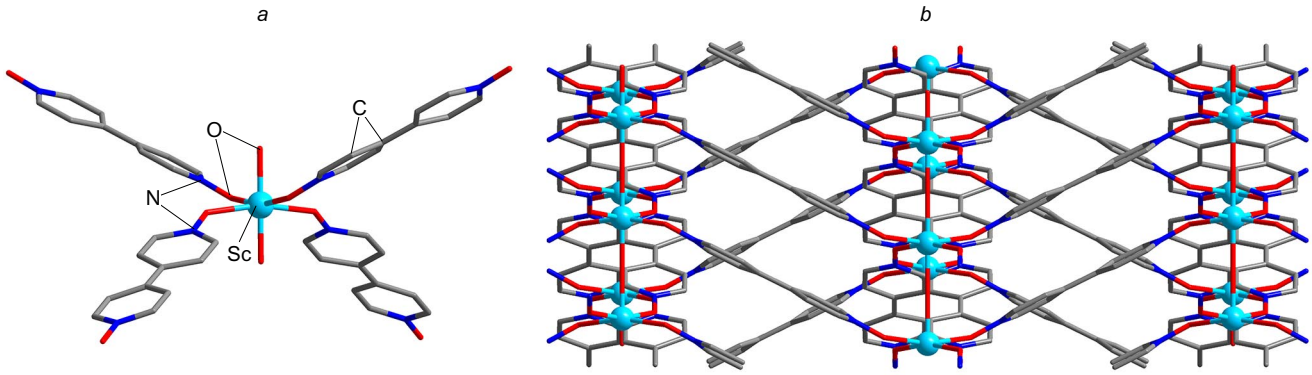


Figure 41. Coordination environment of scandium (*a*) and view along the *b* axis for the structure of $[Sc(bpyO)_4(H_2O)_2](ClO_4)_3$ (**50**) (*b*).[81]

connected into a diamondoid network. The bridging water molecules connect independent diamondoid frameworks into a more complex, fivefold interpenetrated array with $4^8 6^7$ topology (Fig. 41).

5. Conclusion

Scandium(III)-organic frameworks represent a promising class of compounds with unique properties and undisputable advantages over the metal-organic frameworks based on other metal cations. Among them are considerable hydrolytic stability, high thermal stability, pronounced acidic properties and, as a consequence, catalytic activity towards activation of oxygen-containing substrates. Meanwhile, the coordination chemistry of Sc^{III} is generally similar to those of other triply charged metal cations; hence, it is possible not only to transfer the known frameworks to the platform of analogous scandium coordination compounds, but also to obtan mixed-metal frameworks formed like substitution solutions. This approach seems promising for the synthesis of catalytically active metal-organic frameworks, which will be based on abundant metals such as Al^{III}, while the Sc^{III} cation will act as a dopant incorporated into the framework to endow it with the desired catalytic properties.

Despite the advances in the chemistry of scandium(III)-organic frameworks, there are problems related to insufficient elaboration of procedures for the synthesis and activation of this class of frameworks; a more detailed investigation of their functional properties is also required. Even despite the relatively small number of Sc^{III}-based frameworks as compared with other d-element MOFs, systematic consideration of the available structural data presented in this review identifies the key building blocks, topologies and frameworks based on them. Further development of the synthetic approaches and analysis of the relationships between the reaction conditions and product structures would reveal more general trends. Thus, the synthesis, characterization and study of new porous scandium-organic frameworks is of great interest for coordination chemistry, supramolecular chemistry and materials science.

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