Copper(I) and silver(I) coordination frameworks involving extended bipyridazine bridges†

Anna S. Degtyarenko,[a] Pavlo V. Solntsev,[a] Harald Krautscheid,[b]
Eduard B. Rusanov,[c] Alexander N. Chernega[c] and Konstantin V. Domasevitch*[a]

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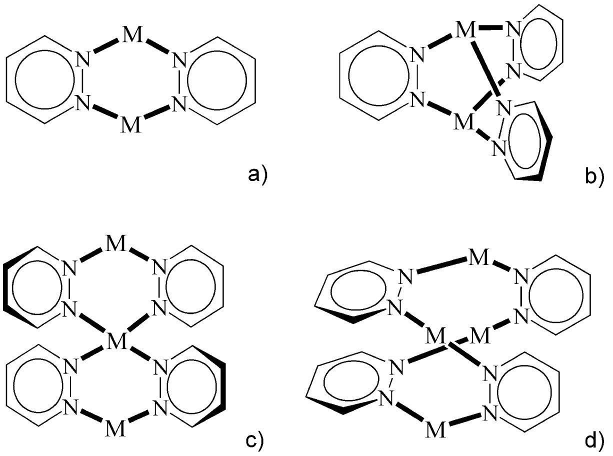
1,4-(Pyridazin-4-yl)benzene (bpph), a new N-donor tetradentate ligand, was prepared by inverse electron demand cycloaddition reacting 1,4-diethynylbenzene and 1,2,4,5-tetrazine. In combination with Cu(I) and Ag(I) ions, it affords coordination framework topologies that were dominated by assembly of dinuclear metal–pyridazine "secondary building blocks" $[M_2(\mu\text{-pdz})_2]$ supporting further polymeric connectivity. In structures $[Cu_2(bpph)(CH_3CN)_2\{S_2O_6\}]$ (**1**) and $[Ag_6(bpph)_3(H_2O)_6\{C_6H_4(COO)_2\}_2]C_6H_4(COO)_2\cdot 4H_2O$ (**8**) interconnection of the dinuclear nodes occurs with anionic dithionate and isophthalate bridges, while $[Ag_2(bpph)\{C_6H_5CO_2\}_2]\cdot 2H_2O$ (**7**) adopts a linear chain structure incorporating disilver(I) pyridazine units and terminal benzoate anions. $[Cu_4(bpph)_5](BF_4)_4\cdot 4CHCl_3$ (**2**) has a 3D supramolecular structure involving polycatenation of the 2D "bilayer" metal–organic topologies built up of five-connected dinuclear nodes. Frameworks of $[Ag(bpph)\{NO_3\}]\cdot CHCl_3$ (**3**) and $[Ag(bpph)\{C_2F_5COO\}]$ (**5**) exist as 2D square-grids nets supported with sets of tetra- and bidentate bipyridazine bridges, while closely related $[Ag_4(bpph)_3\{CF_3COO\}_4]\cdot CH_3CN$ (**4**) is a 1D "ladder" polymer. The three-fold interpenetrated 3D diamondoid framework of $[Ag_4(bpph)_3\{CH_3SO_3\}_4]\cdot 2CHCl_3$ (**6**) was based upon more complicated tetranuclear nodes $[Ag_4(\mu\text{-pdz})_4(pdz)_2]$.

Introduction

The concept of secondary building blocks offers new perspective approaches towards designing of framework coordination polymers.[1] Exploitation of versatile polynuclear metal–organic ensembles as subunits of the framework structures allows generation of unusual coordination topologies,[2] synthesis of porous materials with gas adsorption and catalytic properties[3,4] luminiscent and magnetic coordination polymers,[5] and functionalization of the framework towards interaction with different substrates. The applicable secondary building blocks commonly involve short-distance bridges (hydroxo, oxo, triazole,[6] tetrazolate,[7] carboxylate,[4] and their combinations) between set of metal ions that in total affords very favorable coordination patterns dominating self-assembly processes. Therefore the heteroaryl ligands with multiple N-donor sites possess a special potential for the crystal design as may be compared with a family of simpler connectors derived from monodentate pyridine-N donors.[8,9]

In this respect, pyridazine is very efficient double nitrogen donor ligand towards transition metal ions generating a range of coordination compounds, in which it readily sustains short-distance 1,2-diazine bridges.[10] The latter stabilize proximity of the metal centers and contribute to the formation of complicated polynuclear patterns, as evidenced by characteristic bi- and polynuclear clusters involving either double or triple pyridazine bridges (Scheme 1).[11] Some of the typical M(μ-pdz)M ensembles may retain a set of coordinatively unsaturated positions at the multiple metal centers for interaction with an additional ligands or reaction substrates and they may be applicable for functionalization of the solid-state structure. Features of the metal–pyridazine coordination are especially relevant also from the design perspective, since all of



Scheme 1 Representative polynuclear patterns adopted by pyridazine ligands: (a) dimeric unit; (b) triply-bridged "triptycene-like" unit; (c) spirane motif; (d) tetranuclear "figure eight" stabilized by additional π–π stacking.

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[a] *Inorganic Chemistry Department, Kiev University, Volodimirska Str.64, 01033 Kiev, Ukraine. E-mail: dk@univ.kiev.ua*
[b] *Institut für Anorganische Chemie, Universität Leipzig, Linnéstraße 3, D-04103 Leipzig, Deutschland*
[c] *Institute of Organic Chemistry, Murmanskaya Str.4, 253660 Kiev, Ukraine*

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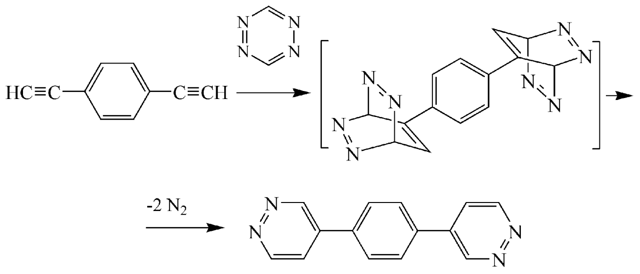
these ensembles may be involved as the "secondary building blocks" for generation of polymeric arrays.[8] In this way, self-assembly reactions between metal ions and bridging ligands possessing multiple pyridazine donor sites provide a clear scenario for construction of the solids integrating polynuclear clusters as an origin of the framework connectivity.

In this context we have examined a new multidentate N-donor 1,4-(pyridazin-4-yl)benzene, which combines abilities for bridging of closely separated and very distal metal ions and in this respect it unites the rich potential of small pyridazine bridges and of longer nitrogen-donor connectors.

Results and discussion

Synthesis of the bis-pyridazine ligand was carried out following a methodology for the inverse electron demand Diels–Alder cycloaddition.[12] Azadiene reactivity of substituted tetrazines allows preparation of different types of pyridazine bridging ligands,[13] while very uncommon use of the parent 1,2,4,5-tetrazine may provide a general convenient route to a series of 3,6-unsubstituted species (Scheme 2). The latter are of special interest as very useful polydentate ligands for copper(I) and silver(I) ions, which possess an appreciable affinity towards multiple N-donor heterocycles.[10,14]

Thus, the structure of the 1,4-(pyridazin-4-yl)benzene (bpph) coordination polymers was typically supported by formation of dinuclear metal–pyridazine ensembles, which provide further connectivity as a "secondary building block". In the structure of dithionate complex $[Cu_2(bpph)(CH_3CN)_2\{S_2O_6\}]$ (**1**) pairs of the copper(I) ions were connected by tetradentate organic bridges into chains. The ligand lies across a center of inversion and the dithionate anion lies across a twofold axis. Typical tetrahedral coordination of the metal ions was completed with the dithionate oxygen atoms and terminal acetonitrile ligands (Table 1). The dithionate groups are coordinated and moreover, their bidentate-bridging function results in interconnection of the metal–organic chains and generation of a flat 2D framework (Fig. 1). There are only two precedents for coordination polymers based upon simple copper(I)–pyridazine dimers, in a combination with octamolybdate or cyanide bridges.[15] The manifestation of nucleophilic properties of the $S_2O_6^{2-}$ groups towards Cu^I cations is slightly unexpected and the complex **1** represents a first example of such coordination. Very recently, dithionate bridges were employed for the construction of Cu^{2+}, Co^{2+} and Zn^{2+} coordination polymers.[16]



Scheme 2 Synthesis of the 1,4-(pyridazin-4-yl)benzene (bpph) involving cycloaddition of bifunctional ethyne and 1,2,4,5-tetrazine.

Table 1 Selected bond distances (Å) and angles (°) for complexes **1** and **2**

$[Cu_2(bpph)(CH_3CN)_2\{S_2O_6\}]$ (**1**)			
Cu1–N1	2.047(2)	Cu1–N3	1.958(2)
Cu1–N2a	1.979(2)	Cu1–O1	2.189(2)
N1–Cu1–N3	102.48(8)	N1–Cu1–O1	100.53(7)
N1–Cu1–N2a	123.02(6)	N3–Cu1–O1	102.02(7)
N3–Cu1–N2a	123.47(8)	N2a–Cu1–O1	100.67(6)

a: $-x$, $1 - y$, $1 - z$.

$[Cu_4(bpph)_5](BF_4)_4{\cdot}4CHCl_3$ (**2**)			
Cu1–N5	2.071(3)	Cu2–N1	1.996(3)
Cu1–N9	2.059(3)	Cu2–N6	2.036(3)
Cu1–N3b	2.005(3)	Cu2–N7a	2.054(3)
Cu1–N8a	2.044(3)	Cu2–N10	2.067(3)
N5–Cu1–N9	98.94(13)	N1–Cu2–N6	120.11(12)
N5–Cu1–N3b	112.24(12)	N1–Cu2–N10	113.55(13)
N5–Cu1–N8a	108.84(12)	N1–Cu2–N7a	111.49(13)
N9–Cu1–N8a	102.04(13)	N6–Cu2–N10	96.61(13)
N3b–Cu1–N8a	117.37(12)	N6–Cu2–N7a	111.14(12)
N9–Cu1–N3b	115.45(13)	N10–Cu2–N7a	101.56(13)

a: x, $1 + y$, z; b: $-1 + x$, y, $-1 + z$.

Rational evolution of the dinuclear copper–pyridazine pattern was observed in the structure of tetrafluoroborate $[Cu_4(bpph)_5](BF_4)_4{\cdot}4CHCl_3$ (**2**). Weak coordinating properties of BF_4^- are reflected by elimination of the anions from the metal environment and this makes possible to involve an additional pyridazine bridge yielding a triptycene-like pattern,

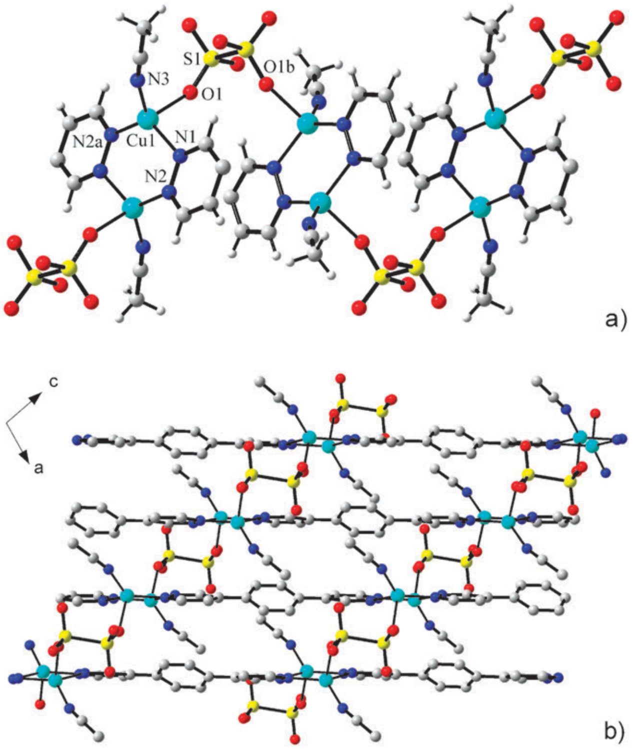


Fig. 1 Structure of $[Cu_2(bpph)(CH_3CN)_2\{S_2O_6\}]$ (**1**): (a) cross-linking of dicopper/dipyridazine units by the dithionate anions; (b) resulting 2D framework incorporating Cu/bipyridazine chains.

which incorporates a pair of copper ions triply bridged by pyridazine (Scheme 1(b)). This characteristic copper(I)–pyridazine motif allows accommodation of two additional ligands (such as acetonitrile or benzonitrile)[17,18] completing the tetrahedral environment of the metal ions. In the present case these two additional coordination sites were occupied by monodentate pyridazine-N donors (Fig. 2(a)) and therefore the dicopper secondary building block could serve as an origin of connectivity for generation of a five-connected framework. The overall topology, however, is not an evident "pillared honeycomb net" and it was dominated by a conformational flexibility of the long organic connector. Thus, a primary connectivity based upon entirely the μ_4-organic bridges is a 1D "ladder" motif, which was further interconnected by *N*,*N*′-bidentate bipyridazine molecules yielding a five-connected bilayer (Fig. 3). This topology itself has little precedent: it is observed in $[Ag(pz)_2][Ag_2(pz)_5](PF_6)_3$ (pz = pyrazine) complex[19] and several systems with 4,4′-bipy and 4,4′-bipy di-*N*-oxide.[20] Within the bilayer, the separation between two interconnected layers is *ca.* 14.1 Å and the bilayer has a significant size of the internal channels (9 × 12 Å, calculated using PLATON[21]). Therefore, free space in such structure is partially filled by parallel polycatenation[22] of the bilayers (Fig. 4), which in total occupy 57.5% of the crystal volume.[21] The remaining space is filled with counter anions and guest chloroform molecules.

Formation of the dimeric metal–pyridazine cycles was also a well-predictable feature for silver(I) compounds and such the coordination moieties may be best involved as "secondary building blocks". Complexes with low nucleophilic NO_3^-, CF_3COO^- and $C_2F_5COO^-$ anions were closely related to the above examples and they illustrate utility of the coordination pattern for the generation of frameworks (Table 2). Thus, in the nitrate compound $[Ag(bpph)\{NO_3\}]\cdot CHCl_3$ (**3**) the disilver–pyridazine chains remain as a clearly distinguishable motif of the structure (Fig. 5). The nitrate groups are only weakly coordinated (Ag–O 2.66, 2.69 Å) and this makes possible coordination of the extra pyridazine-N donors (unlike simpler dimeric molecular units in the complex of parent pyridazine $[Ag(pdz)\{NO_3\}]_2$).[23] This additional set of the

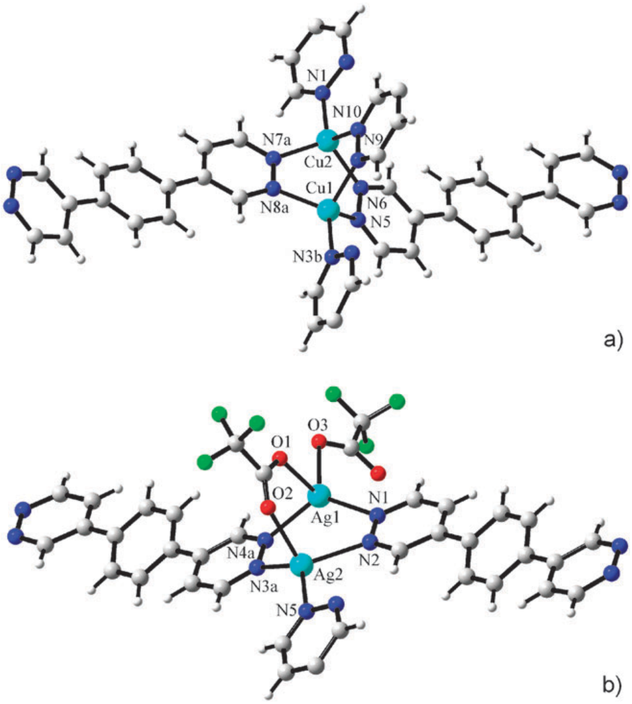


Fig. 2 Illustrative types of dinuclear units constituting the framework nodes: (a) triple pyridazine bridge between the copper(I) ions in structure **2**; (b) combination of double pyridazine and carboxylate bridges between silver ions in structure **4**.

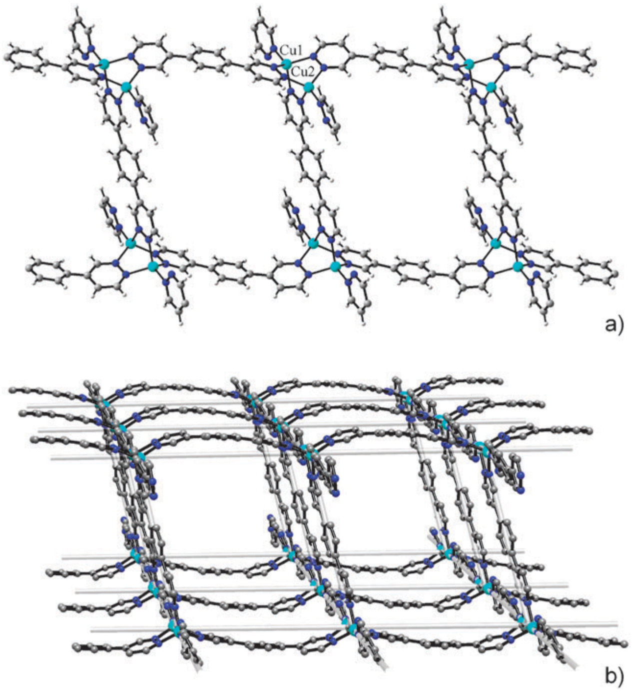


Fig. 3 (a) 1D "ladder" motif of structure **2** assembled by linking of the dicopper units by μ_4-bipyridazine bridges (one of two unique tetradentate bipyridazine molecules lies across an inversion centre), while additional bidentate ligands interconnect the ladders orthogonal to the drawing plane; (b) resulting coordination bilayer involving five-connected nodes.

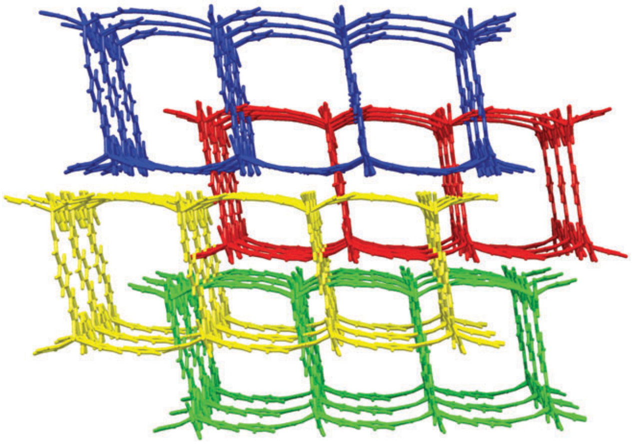


Fig. 4 Parallel polycatenation of the 2D bilayers in structure **2**, leaving only small channels (3 × 5 Å) for housing of guest chloroform molecules and counter anions.

Table 2 Selected bond distances (Å) and angles (°) for complexes **3–6**

$[Ag(bpph)\{NO_3\}]\cdot CHCl_3$ (**3**)			
Ag1–N1	2.350(3)	Ag1–O1	2.661(2)
Ag1–N2a	2.259(2)	Ag1–O3	2.691(3)
Ag1–N3	2.352(3)		
N1–Ag1–N3	102.76(9)	N2a–Ag1–O1	101.79(8)
N1–Ag1–N2a	114.66(9)	N2a–Ag1–O3	127.22(9)
N1–Ag1–O1	128.16(8)	N3–Ag1–O1	76.65(8)
N1–Ag1–O3	80.61(8)	N3–Ag1–O3	88.66(8)
N2a–Ag1–N3	130.49(9)	O1–Ag1–O3	47.67(7)
a: $-x$, $1-y$, $2-z$.			
$[Ag_4(bpph)_3\{CF_3COO\}_4]\cdot CH_3CN$ (**4**)			
Ag1–N1	2.288(2)	Ag2–N2	2.347(2)
Ag1–N4a	2.317(2)	Ag2–N5	2.287(2)
Ag1–O1	2.481(3)	Ag2–N3a	2.304(2)
Ag1–O3	2.401(3)	Ag2–O2	2.374(3)
N1–Ag1–N4a	122.97(8)	N5–Ag2–N3a	127.43(8)
N1–Ag1–O3	122.88(10)	N5–Ag2–N2	101.36(8)
N1–Ag1–O1	102.42(9)	N5–Ag2–O2	103.71(11)
N4a–Ag1–O1	93.55(9)	N3a–Ag2–N2	122.90(8)
N4a–Ag1–O3	108.36(11)	N3a–Ag2–O2	93.71(11)
O3–Ag1–O1	97.33(12)	N2–Ag2–O2	102.41(9)
a: $1-x$, $1-y$, $1-z$.			
$[Ag(bpph)\{C_2F_5COO\}]$ (**5**)			
Ag1–N1	2.343(2)	Ag1–N3	2.341(3)
Ag1–N2a	2.304(3)	Ag1–O1	2.388(2)
N1–Ag1–N3	126.20(9)	N2a–Ag1–N3	108.01(9)
N1–Ag1–N2a	113.36(9)	N2a–Ag1–O1	113.85(9)
N1–Ag1–O1	101.95(9)	N3–Ag1–O1	90.87(9)
a: $-x$, $-y$, $1-z$.			
$[Ag_4(bpph)_3\{CH_3SO_3\}_4]\cdot 2CHCl_3$ (**6**)			
Ag1–N1	2.202(7)	Ag3–N4b	2.254(8)
Ag1–N7a	2.213(7)	Ag4–N3b	2.250(8)
Ag2–N2	2.306(7)	Ag4–N8a	2.310(7)
Ag2–N5	2.242(7)	Ag4–N11c	2.341(10)
Ag2–N9	2.338(9)	Ag–O	2.40(1)–2.58(1)
Ag3–N6	2.255(8)		
N1–Ag1–N7a	166.8(3)	N6–A–g3–N4b	147.0(3)
N2–Ag2–N9	98.1(3)	N3b–Ag4–N8a	129.3(3)
N5–Ag2–N2	129.4(3)	N3b–Ag4–N11c	127.4(4)
N5–Ag2–N9	124.4(3)	N8a–Ag4–N11c	99.1(4)
a: $-x$, $-y$, $1-z$; b: $1-x$, $-y$, $-z$; c: $-1+x$, $0.5-y$, $-0.5+z$.			

bidentate organic ligands was employed for the cross-linking of the chains and this yields a 2D "square-grid" polymeric structure. The bidentate bpph group adopts slightly unexpected 2,2′-like coordination, which allows to bridge Ag atoms at a shorter distance of 13.71 Å (*cf. ca.* 16 Å for 1,1′-bidentate coordination) and to minimize the size of the square meshes. The net nodes for such the framework are composed by $[Ag_2(\mu\text{-}pdz)_2(pdz)_2]$ fragments, which are stabilized by a pair of weak CH···N hydrogen bonds and itself are very characteristic for silver–pyridazine or phthalazine coordination.[24]

A very comparable principle of the network architecture was observed also for the $[Ag(bpph)\{C_2F_5COO\}]$ (**5**) complex (Fig. 5(b)). Needs for incorporation of bulk pentafluoropropionate groups effect augmentation of the net meshes, which was achieved with 1,1′-bridging mode of the bidentate molecules of the ligand (Ag–Ag 16.03 Å). That the coordination topology is very sensitive to the steric volume of functionally almost uniform counter anions was best illustrated by structure of trifluoroacetate $[Ag_4(bpph)_3\{CF_3COO\}_4]\cdot CH_3CN$ (**4**). This structure was also based upon "disilver chains" involving organic ligands as μ_4-bridges. However, one of the carboxylate anions was bidentate-bridging within the disilver unit (in this respect the structure of the $Ag_2(pyridazine)_2(\mu\text{-}CF_3COO)$ framework parallels the $Cu_2(pyridazine)_3$ unit observed in structure **2**), while a second trifluoroacetate group was monodentate and terminal (Fig. 2(b)). Such bridging coordination of the trifluoroacetate contributes to the proximity of two sliver ions (Ag···Ag 3.279 Å *vs.* 3.785 and 3.842 Å for **5** and **3**, respectively). This may be compared with a very short argentophilic interaction in dimeric silver(I) trifluoroacetate itself (2.973 Å).[25] Unlike the nitrate (**3**) and pentafluoropropionate (**5**) structures, the disilver unit in **4** retains only one coordinatively unsaturated position for accommodation of an additional monodentate pyridazine donor and thus it provides only a three-connected node for the network. The latter is one-dimensional and exists in the form of a "ladder" (Fig. 6).

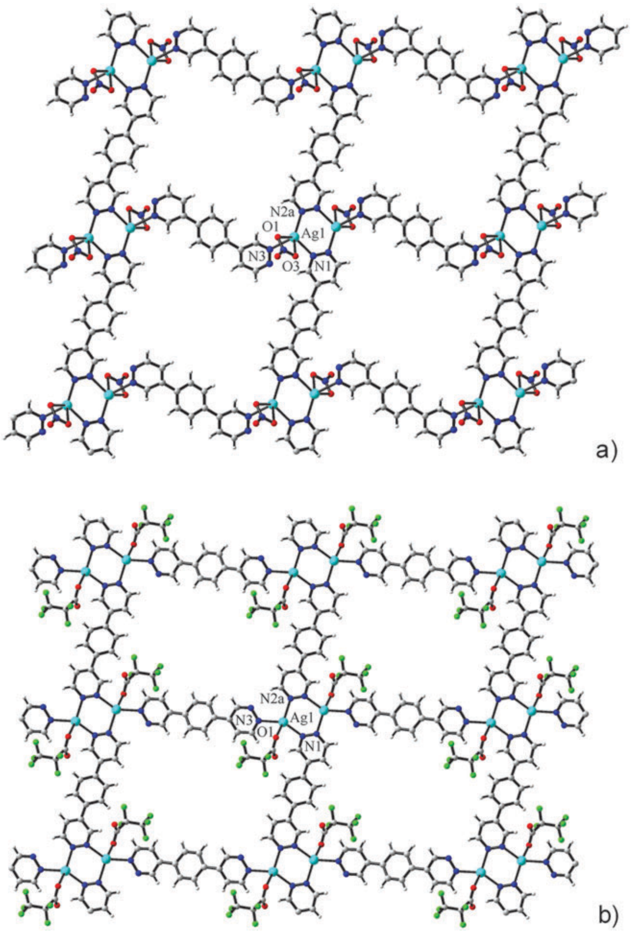


Fig. 5 Closely related structure of 2D coordination frameworks **3** (a) and **5** (b): cross-linking of the disilver/pyridazine chains by a set of bidentate ligand molecules. Note differences in the coordination mode of the μ_2-ligand, which allows tuning of the shape and size of the resulting rectangular meshes of the framework. In these structures, either bi- or tetradentate ligand molecules are situated across inversion centres.

Complex $[\mathrm{Ag_4(bpph)_3\{CH_3SO_3\}_4}]\cdot 2\mathrm{CHCl_3}$ (**6**) reveals a more complicated metal–ligand pattern composed with four silver ions, four μ-pyridazine moieties and two additional monodentate pyridazine-N donors, in the form of "figure eight" (Scheme 1(d)). The structure of such a tetranuclear "secondary building block" is very favorable since it allows slipped π–π stacking interactions[26] within the pairs of parallel pyridazine cycles (Fig. 7). These interactions occur at distances (centroid–centroid separations 3.58 and 3.64 Å), which are consistent with typical Ag···Ag contacts and in view of combination of coordination and stacking interactions the components afford a complementary system. A similar pattern involving six μ-pyridazine groups was observed also for a simpler 4,4′-bipyridazine ligand[8] and in a mixed-ligand pyridazine/3,5-bis(trifluoromethyl)pyrazolate complex.[11a] For the resulting tetrasilver square, each of the edges was centered by coordinating methanesulfonate groups, which bridge the adjacent metal ions with very long Ag–O bonds. Thus pairs of the μ$_4$-ligand molecules connect Ag$_4$ ensembles into the dimeric chains, while a set of bidentate organic bridges links the chains into the very distorted diamondoid framework. This adopts three-fold class Ia interpenetration[27] where the identical nets are related by a single translation vector.

Another possibility for interconnection of the disilver secondary building blocks arises in a doubling of the anion functionality, as it may be found from comparison of carboxylate structures **7** and **8**. The simpler structural prototype was provided by benzoate complex $[\mathrm{Ag_2(bpph)\{C_6H_5CO_2\}_2}]\cdot 2\mathrm{H_2O}$ (**7**), which adopts a 1D chain-like array incorporating disilver(I) pyridazine units (Fig. 8). Each of the heterocyclic termini is bidentate-bridging and the entire ligand is a tetradentate bridge. The nucleophilic carboxylate anions are situated coplanar towards the disilver units and are coordinated in a bidentate pseudochelate fashion (Ag–O 2.38, 2.67 Å) (Table 3), similarly to silver(I) acetate complex with phthalazine.[28] This terminates any further coordination connectivity, while the interchain interactions occur by means of hydrogen bonding of the carboxylate groups with the solvate water molecules (O···O 2.67, 2.81 Å).

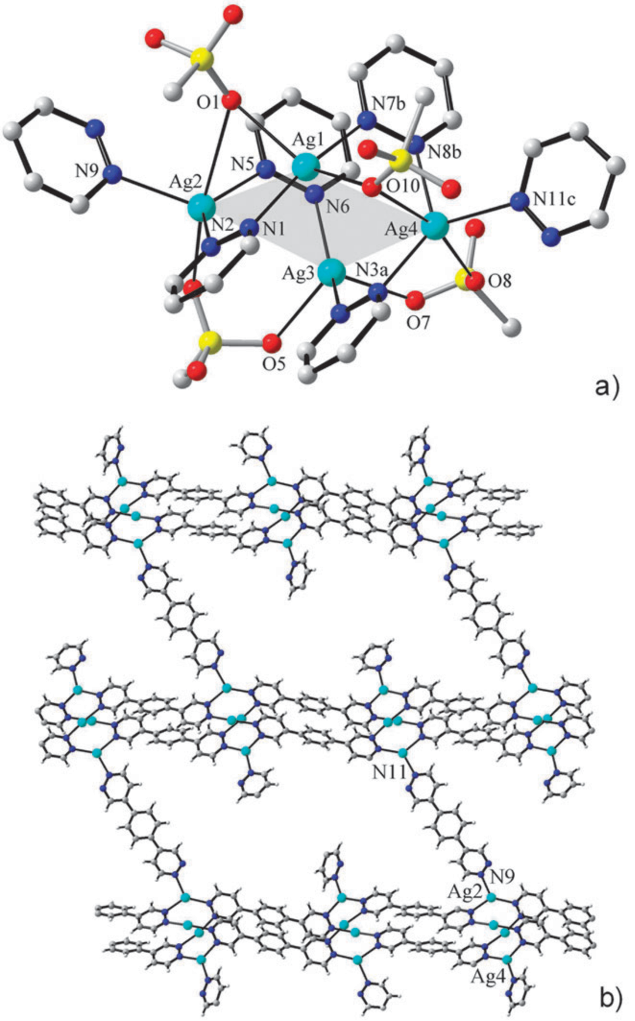


Fig. 7 (a) Tetranuclear silver–pyridazine cluster providing the network nodes in structure **6**. Note the close parallel alignment of the pairs of pyridazine cycles supporting weak slipped π–π stacking; (b) Fragment of the polymer showing mode of cross-linking of the silver/bipyridazine double chains by additional bidentate ligand molecules.

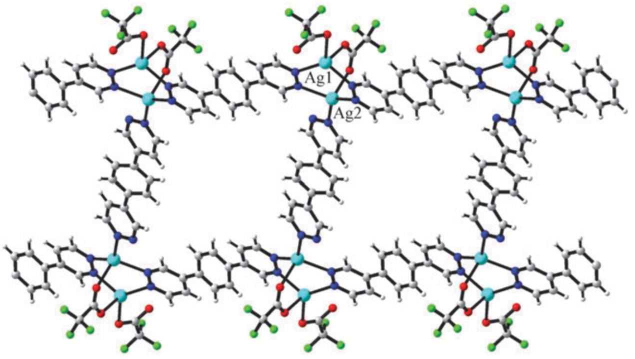


Fig. 6 One-dimensional "ladder" coordination polymer $[\mathrm{Ag_4(bpph)_3\{CF_3COO\}_4}]\cdot\mathrm{CH_3CN}$ (**4**). The bidentate bipyridazine ligand is situated across an inversion centre. Space within the rectangular windows of the motif is populated by trifluoroacetate groups of the adjacent "ladder".

As a further step for construction of the framework, the interconnection of the disilver–pyridazine chains may be achieved by simple doubling the carboxylate function of the counter-anion and this suggests utility of the above silver–pyridazine–carboxylate array as a "supramolecular synthon". In this way, the two-dimensional structure of the isophthalate complex $[\mathrm{Ag_6(bpph)_3(H_2O)_6\{C_6H_4(CO_2)_2\}_2}]\mathrm{C_6H_4(CO_2)_2}\cdot 4\mathrm{H_2O}$ (**8**) was clearly derived from the 1D chains of parent benzoate prototype, although only one of three unique silver ions completely retains the above coordination environment involving a pseudochelating carboxylate group (Ag1–O 2.43, 2.62 Å) (Fig. 9). The second carboxylate group of the dianion was coordinated monodentately, similarly to the silver phthalate complex with phthalazine,[29] and the tetrahedral environment of the silver ion Ag2 was completed with a water molecule, while the third silver ion coordinates two terminal aqua ligands. The latter eliminates part of the carboxylate bridges and this results in a formation of 3,4-connected flat cationic net (Schläfli symbol $(4.6^2)2(4^2;6^2)$) instead of the evident 4-connected neutral framework. Non-coordinated

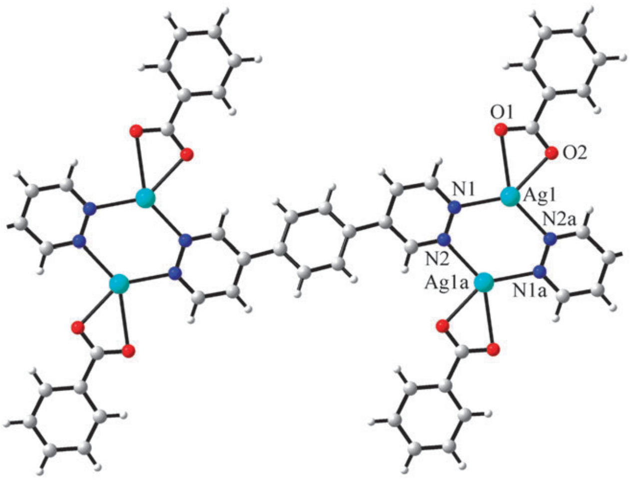


Fig. 8 One-dimensional disilver/bipyridazine chain in the structure of benzoate complex **7**. The pyridazine ligands and disilver/pyridazine dimers are situated across inversion centres.

isophthalate dianions populate voids of the structure and are involved in extensive hydrogen bonding.

Experimental

All chemicals were of analytical grade and used as received without further purification. Unsubstituted 1,2,4,5-tetrazine was prepared following a detailed procedure described in a supplementary publication.[9]

Preparation of 1,4-(pyridazin-4-yl)benzene

A solution of 2.30 g (0.028 mol) 1,2,4,5-tetrazine and 1.76 g (0.014 mol) 1,4-diethynylbenzene in 40 ml of dry dioxane was stirred at 80 °C until evolution of nitrogen gas ceased (20–25 h). The precipitate was filtered off, washed with dioxane and diethyl ether and dried in air. Yield of practically pure colorless crystalline product was 2.95 g (90%). The compound is sparingly soluble in methanol and chloroform. ^{1}H NMR (dmso-d$_6$, δ/ppm, J/Hz): 8.08 (s, 4H, C_6H_4), 8.02 (d, 2H, 5-H-pdz, J = 5.21), 9.26 (d, 2H, 6-H-pdz, J = 5.21), 9.64 (s, 2H, 3-H-pdz).

Coordination compounds were synthesized reacting the components in acetonitrile–chloroform solutions, using the layering technique. Starting copper(I) compounds, dithionate and tetrafluoroborate, were generated in a dilute acetonitrile solution by reduction of corresponding copper(II) salts with an excess of copper powder. Colorless solutions containing $[Cu(CH_3CN)_4]X$ (X = BF_4, 1/2S_2O_6) are relatively air-stable and they were used for preparation of coordination polymers without isolation of individual copper(I) salts. Silver benzoate and isophthalate complexes **7** and **8** were prepared from aqueous solutions using a hydrothermal technique.

Preparation of $[Cu_2(bpph)(CH_3CN)_2\{S_2O_6\}]$ (1)

A solution of 66.3 mg (0.2 mmol) $CuS_2O_6{\cdot}6H_2O$ in 4 ml acetonitrile was stirred with 127 mg (2 mmol) of copper powder for 1 h, until a total discoloration of the solution was observed. The solution was filtered and then layered over the solution of the ligand (23.4 mg, 0.1 mmol) in 8 ml chloroform. 8 ml of a chloroform–acetonitrile mixture (1 : 1 v/v) was introduced as an intermediate layer. Slow interdiffusion of the solutions over 15 d led to crystallization of orange–red plates of the product (45 mg, 75%). Anal. for **1**, $C_{18}H_{16}Cu_2N_6O_6S_2$. Calc. (%): C, 35.82; H, 2.67; N, 13.93. Found (%): C, 35.70; H, 2.49; N, 14.09.

Table 3 Selected bond distances (Å) and angles (°) for complexes **7** and **8**

$[Ag_2(bpph)\{C_6H_5CO_2\}_2]{\cdot}2H_2O$ (**7**)			
Ag1–N1	2.253(2)	Ag1–O1	2.673(2)
Ag1–N2a	2.335(2)	Ag1–O2	2.379(2)
N1–Ag1–N2a	122.96(8)	N2a–Ag1–O1	143.53(8)
N1–Ag1–O1	92.92(8)	N2a–Ag1–O2	92.52(8)
N1–Ag1–O2	144.38(8)	O2–Ag1–O1	51.47(7)
a: −x, −y, 1 − z.			
$[Ag_6(bpph)_3(H_2O)_6\{C_6H_4(CO_2)_2\}_2]C_6H_4(CO_2)_2{\cdot}4H_2O$ (**8**)			
Ag1–N2	2.342(3)	Ag2–O4	2.321(3)
Ag1–N4	2.294(4)	Ag2–O7	2.621(5)
Ag1–O1	2.431(4)	Ag3–N1	2.298(4)
Ag1–O2	2.622(4)	Ag3–N3	2.243(3)
Ag2–N5	2.333(4)	Ag3–O5	2.471(4)
Ag2–N6a	2.256(3)	Ag3–O6	2.427(4)
N2–Ag1–N4	125.69(14)	N6a–Ag2–O4	137.37(15)
N2–Ag1–O1	85.07(13)	O4–Ag2–O7	96.65(18)
N4–Ag1–O1	139.53(14)	N1–Ag3–N3	128.87(14)
N4–Ag1–O2	96.47(12)	N1–Ag3–O5	133.57(14)
O1–Ag1–O2	52.20(12)	N1–Ag3–O6	88.73(14)
N5–Ag2–N6a	123.54(14)	N3–Ag3–O6	125.76(14)
N5–Ag2–O4	95.17(14)	N3–Ag3–O5	91.29(13)
N5–Ag2–O7	115.01(19)	O6–Ag3–O5	82.98(14)
N6a–Ag2–O7	83.39(15)		
a: −x, −1 − y, −1 − z.			

Complex $[Cu_4(bpph)_5](BF_4)_4{\cdot}4CHCl_3$ (**2**) (dark-red blocks) was synthesized similarly, starting with an acetonitrile solution of copper(I) tetrafluoroborate. Crystals of the compound easily lose solvate chloroform molecules in air within minutes, which was accompanied with a loss of crystallinity.

Preparation of $[Ag(bpph)\{NO_3\}]{\cdot}CHCl_3$ (3)

A solution of $AgNO_3$ (17.0 mg, 0.10 mmol) in 3 ml acetonitrile was layered over the solution of ligand L (23.4 mg, 0.10 mmol) in 8 ml chloroform. Light-yellow prisms of the product grew on the walls of the tube as the reaction layers slowly interdiffused (14–15 d). The yield was 44.5 mg, 85%. The sample is stable under the mother-liquor, but it loses the incorporated solvent in air with loss of crystallinity. Anal. for **3**, $C_{15}H_{11}AgCl_3N_5O_3$. Calc. (%): C, 34.41; H, 2.12; N, 13.38. Found (%): C, 34.76; H, 2.31; N, 13.62.

Coordination polymers $[Ag_4(bpph)_3\{CF_3COO\}_4]{\cdot}CH_3CN$ (**4**) (yellow blocks, yield 55%), $[Ag(bpph)\{C_2F_5COO\}]$ (**5**) (pale yellow plates, yield 70%) and $[Ag_4(bpph)_3\{CH_3SO_3\}_4]{\cdot}2CHCl_3$ (**6**) (light-yellow prisms, yield 45%) were prepared similarly starting with the corresponding silver(I) salts. Anal. for **4**, $C_{52}H_{33}Ag_4F_{12}N_{13}O_8$. Calc. (%): C, 38.38; H, 2.04; N, 11.19. Found (%): C, 38.12; H, 2.01; N, 11.03. Anal. for **5**, $C_{17}H_{10}AgF_5N_4O_2$. Calc. (%): C, 40.42; H, 2.00; N, 11.09. Found (%): C, 40.31; H, 1.83; N, 11.24.

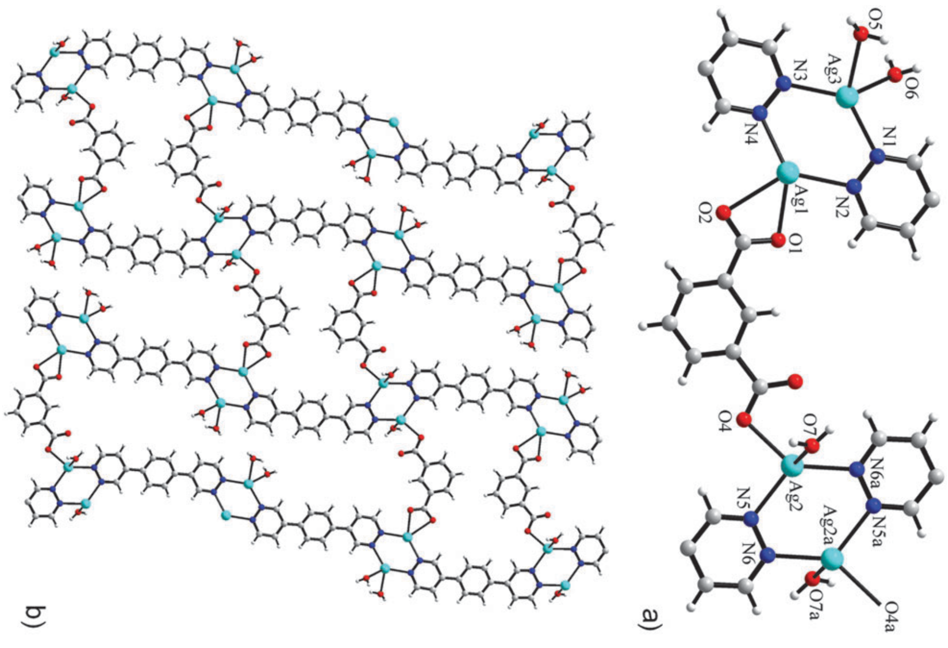


Fig. 9 (a) Three types of silver coordination environments in the structure **8**, one of which involves two terminal aqua ligands; (b) resulting 2D coordination 3,4-connected net based upon interconnection of the disilver–pyridazine chains with isophthalate anions. One of two unique bipyridazine ligands is situated across an inversion centre.

Preparation of $[Ag_2(bpph)\{C_6H_5CO_2\}_2]\cdot 2H_2O$ (7)

Silver(I) benzoate (32.1 mg, 0.14 mmol), ligand (16.4 mg, 0.07 mmol) and 6 ml of water were sealed in a Pyrex glass tube. The mixture was heated at 180 °C in a glycerine-bath for 8 h and then it was cooled to r.t. over 40 h. Large yellow–green crystals of the complex were separated in an almost quantitative yield of 44.8 mg (94%). Anal. for **7**, $C_{28}H_{24}Ag_2N_4O_6$. Calc. (%): C, 46.18; H, 3.32; N, 7.70. Found (%): C, 46.52; H, 3.28; N, 7.84.

Isophthalate complex $[Ag_6(bpph)_3(H_2O)_6\{C_6H_4(CO_2)_2\}_2]\cdot C_6H_4(CO_2)_2\cdot 4H_2O$ (**8**) (yellow plates, yield 85%) was prepared in a similar way, starting with a mixture of silver acetate (20.0 mg, 0.12 mmol) and isophthalic acid (11.6 mg, 0.07 mmol). Anal. for **8**, $C_{66}H_{62}Ag_6N_{12}O_{22}$. Calc. (%): C, 39.19; H, 3.09; N, 8.31. Found (%): C, 39.45; H, 2.98; N, 8.47.

Crystallography

Crystallographic measurements were made using a Stoe Imaging Plate Diffraction System (213 K, absorption corrections using DIFABS) and Bruker APEX area-detector diffractometer for **3**, **6** and **7** (296 and 213 K, absorption corrections by SADABS[30]) (Mo-Kα radiation, λ = 0.71073 Å). The

Table 4 Crystal data for $[Cu_2(bpph)(CH_3CN)_2\{S_2O_6\}]$ (**1**), $[Cu_4(bpph)_5](BF_4)_4\cdot 4CHCl_3$ (**2**), $[Ag(bpph)\{NO_3\}]\cdot CHCl_3$ (**3**), $[Ag_4(bpph)_3\{CF_3CO_2\}_4]\cdot CH_3CN$ (**4**), $[Ag(bpph)\{C_2F_5CO_2\}]$ (**5**), $[Ag_4(bpph)_3\{CH_3SO_3\}_4]\cdot 2CHCl_3$ (**6**), $[Ag_2(bpph)\{C_6H_5CO_2\}_2]\cdot 2H_2O$ (**7**) and $[Ag_6(bpph)_3(H_2O)_6\{C_6H_4(CO_2)_2\}_2]C_6H_4(CO_2)_2\cdot 4H_2O$ (**8**)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{18}H_{16}Cu_2N_6O_6S_2$	$C_{74}H_{54}B_4Cl_{12}Cu_4F_{16}N_{20}$	$C_{15}H_{11}AgCl_3N_5O_3$	$C_{52}H_{33}Ag_4F_{12}N_{13}O_8$	$C_{17}H_{10}AgF_5N_4O_2$	$C_{48}H_{44}Ag_4Cl_6N_{12}O_{12}S_4$	$C_{28}H_{24}Ag_2N_4O_6$	$C_{66}H_{62}Ag_6N_{12}O_{22}$
M	603.57	2250.17	523.51	1627.39	505.16	1753.37	728.25	2022.50
T/K	213	213	296	223	213	213	296	213
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group, Z	$C2/c$, 4	$P\bar{1}$, 1	$P\bar{1}$, 2	$P\bar{1}$, 1	$P\bar{1}$, 2	$P2_1/c$, 4	$P2_1/c$, 2	$P\bar{1}$, 1
a/Å	9.3471(6)	12.5703(9)	8.3964(2)	10.9059(10)	5.5566(7)	19.3101(19)	7.2863(3)	9.4238(6)
b/Å	18.9283(11)	13.7895(13)	9.5399(2)	11.1531(11)	10.5875(13)	17.3714(15)	14.3867(6)	14.2038(12)
c/Å	12.4791(9)	14.1629(12)	12.4383(3)	13.8012(13)	15.419(2)	18.1903(15)	12.2774(5)	14.2032(10)
α/°	90	94.203(11)	80.0470(10)	92.620(11)	72.987(10)	90	90	104.457(8)
β/°	101.718(8)	93.205(11)	82.900(2)	108.916(11)	84.721(11)	99.346(5)	90.945(3)	98.140(8)
γ/°	90	107.835(10)	64.9520(10)	117.522(10)	82.058(11)	90	90	108.924(9)
U/Å^3	2161.9(3)	2322.8(3)	887.61(4)	1369.6(3)	857.81(19)	6020.8(9)	1286.81(9)	1689.3(3)
μ(Mo-Kα)/mm^{-1}	2.212	1.334	1.615	1.518	1.250	1.757	1.574	1.794
D_c/g cm^{-3}	1.854	1.609	1.959	1.973	1.956	1.934	1.880	1.988
θ_{max}/°	28.12	27.08	26.42	28.15	28.20	25.35	26.54	27.09
Meas./unique reflns	9065/2606	19140/10016	9394/3592	12755/6582	6535/4169	25245/10705	8074/2634	11283/7302
R_{int}	0.033	0.056	0.035	0.034	0.025	0.068	0.035	0.049
Params refined	154	576	244	469	262	713	190	541
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.029, 0.074	0.055, 0.155	0.035, 0.070	0.030, 0.076	0.032, 0.072	0.093, 0.242	0.033, 0.069	0.049, 0.120
Goof on F^2	0.968	0.921	1.057	0.897	0.850	1.088	1.048	0.879
Max., min. peak/e Å^{-3}	0.63, −0.43	0.89, −0.68	0.44, −0.55	0.76, −0.61	0.62, −0.51	0.98, −1.87	0.32, −0.65	1.52, −1.29

structures were solved by direct methods using the program SHELXS-97.[31] The refinement and all further calculations were carried out using SHELXL-97.[31] The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 (Table 4). For all structures CH hydrogens were added geometrically, OH hydrogen atoms of coordinated water molecules were located and then fixed. In structure **2**, both unique solvate chloroform molecules are disordered, the components of the disorder were refined isotropically and with restraints in their geometry. In trifluoroacetate structure **4**, both independent CF_3 groups show typical rotational disorder, which was resolved with fixed geometry and with partial occupancies 0.5, 0.5 and 0.6, 0.4. Solvate acetonitrile molecule was equally disordered over the center of inversion, it was refined anisotropically and the CH_3 hydrogen atoms were not added. In **8**, 2-aromatic carbon atom of the non-coordinated isophthalate dianion occupies an inversion centre and therefore the entire anion is disordered over two partially overlapping positions. The disorder was resolved with fixed geometry of carboxylate groups. Non-coordinated water molecules were also equally disordered, they were refined isotropically and the hydrogen atoms were not added. Two independent chloroform molecules in structure **6** were badly disordered and therefore the remaining electron density was modeled using Squeeze.[21] One of the methanesulfonate anions was equally disordered over two overlapping positions. It was possible to resolve the disordering scheme with fixed geometry. Graphical visualisation of the structures was made using the Diamond program.[32]

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b801231h

Conclusions

The study provides a novel tetradentate ligand system, which is well suited for bridging of many metal ions and generation of metal–organic polymer structures. Our results suggest utility of the metal ion/pyridazine dimers as attractive "secondary building units" for the rational construction of coordination framework solids. The very easy and general synthetic route employed for preparation of the extended bipyridazine ligand may find further applications for developing of multidentate organic building blocks for crystal design.

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