The novel metalloligand \([\text{Fe(bppd)}_3]\) (bppd = 1,3-bis(4-pyridyl)-1,3-propanendionate) for the crystal engineering of heterometallic coordination networks with different silver salts. Anionic control of the structures†

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The crystal engineering of heterometallic coordination networks based on the novel tris-chelate metalloligand \([\text{Fe}}^{iii}(\text{bppd})_3]\) (bppd = 1,3-bis(4-pyridyl)-1,3-propanendionate) is reported here. The building block \([\text{Fe(bppd)}_3]\) crystallizes with a balanced packing of the \(\Delta\) and \(\Lambda\) forms and exhibits distorted octahedral chiral structure with six exo-oriented pyridyl donor groups suitable for networking via interactions with external metal ions. It was reacted with many silver salts \(\text{AgX} (X = \text{BF}_4^-, \text{ClO}_4^-, \text{PF}_6^-, \text{AsF}_6^-, \text{SbF}_6^-, \text{NO}_3^-, \text{CF}_3\text{SO}_3^-, \text{tosylate})\) giving polymeric products with structures depending on the nature of the counter-ions \(X^-.\) With pseudo-spherical anions (such as \(\text{BF}_4^-\)), \(\text{ClO}_4^-\), \(\text{PF}_6^-\), \(\text{AsF}_6^-\) and \(\text{SbF}_6^-\) 2D polymeric species \([\text{Fe(bppd)}_3\text{Ag}(\text{X})]\) are obtained showing sql topology, because the metalloligands use only four, out of the six pyridyl donors, to bind silver ions. The reaction with \(\text{Ag(CF}_3\text{SO}_3)\) affords a quite different type of \([\text{Fe(bppd)}_3\text{Ag}^+]\) 2D polymeric frame, with the metalloligands that again employ only four pyridyl groups for networking, i.e. a double layered species comprised of two superimposed honeycomb sheets, exhibiting a \((4^1, 6^1)\) topology. By using \(\text{AgNO}_3\) a 3D framework, \([\text{Fe}_2(\text{bppd})_6\text{Ag}_3(\text{NO}_3)_3]\), is obtained that, interestingly, consists of double layers like those of the previous species connected via Ag bridges on both sides to produce a bimodal 5,4-connected 2-fold interpenetrated network. The reaction with silver \(p\)-tolenesulfonate produces the complex 3D nanoporous network \([\text{Fe}_2(\text{bppy})_6\text{Ag}_3(\text{tosylate})]\) with 6-connected metalloligands and 3- and 4-connected silver ions. An interesting rationalization of this network is that it is comprised of 1D parallel nanotubular motifs of hexagonal section with square-meshed walls; these nanotubes are laterally interconnected by Ag triple-bridging atoms to generate the whole 3D array. We observe that in these species the metalloligands use a variable number of pyridyl donors for networking, i.e. four, five and six, leading to frames of increased complexity and dimensionality that are strongly dependent on the anionic shape and nature. The reactions of the analogous metalloligand \([\text{Al}^{iii}(\text{bppd})_3]\) with the same \(\text{AgX}\) salts under similar conditions produce polycrystalline materials that in the cases of silver triflate and tosylate are isostructural with the corresponding iron containing species, as evidenced by their X-ray powder diffraction spectra.

Introduction

A great interest is currently focused on the design of coordination networks/metal–organic frameworks (MOFs)\(^1,2\) because they are promising materials for many potential applications such as gas storage, molecular sensing, separation, ion exchange, catalysis, optics and magnetism.\(^2\) A useful strategy to the rational synthesis of such networked compounds consists in the use of molecular building blocks, in particular those called metalloligands,\(^3-6\) that contain suitably oriented exo-donor groups and therefore able to direct, in principle, the formation of desired polymeric architectures.

The metalloligands can be employed in place of organic ligands to join different metal centers, thus possibly affording heterometallic architectures, which can display novel properties; at difference from the SBU\(\text{s}\) that can be envisaged as fundamental units in the networks assembled via the reticular chemistry approach\(^7,8,9\) the metalloligands are self-existing entities. The stepwise approach implies a careful choice of polyfunctional ligands for the preparation of the discrete...
metal–organic building blocks with a rather rigid and defined stereochemistry. Chelating ligands are frequently employed, which must bear additional outward oriented donor groups, mainly carboxylate, nitrile or pyridyl groups. A number of metalloligands have been employed for this purpose; for instance, tris(dipyrrinato) metal complexes\(^6\) were shown to be a versatile class of metalloligands for the preparation of a variety of interesting MOFs. Functionalised \(\beta\)-diketonato ligands were used as suitable chelating agents for the preparation of metalloligands, both tris-chelated\(^7,8\) and bis-chelated\(^9\) complexes.

In this concern we have already investigated the use of \textit{ad hoc} prepared metalloligands for the engineering of heterometallic networks, such as the complex \textit{trans}-[Ru(pyrazine)\(_2\)Cl\(_2\)] showing four equatorial pyrazine donors,\(^9\) Zn\(^{II}\)-metalated pyridyl-functionalised porphyrins,\(^9\) and the tris-chelate species \([\text{M}^{II}L_3][\text{M} = \text{Fe}^{II} \text{and Co}^{III} \text{and [M}^{II}L_3][\text{M} = \text{Mn}^{II}, \text{Co}^{II}, \text{Zn}^{II}, \text{Cd}^{II}]\) with HL = 1,3-bis(4-cyano-phenyl)-1,3-propanedione.\(^9\)

We report here the synthesis and characterization of the novel tris-chelate metalloligand \([\text{Fe}^{II}(\text{bppd})_3]\) (with \(\text{Hbppd} = 1,3,5\)-tri(pyridyl)-1,3-propanedionato) and it use for the modular engineering of heterometallic MOFs with a variety of Ag\(X\) salts (\(X = \text{BF}_4^{-}, \text{ClO}_4^{-}, \text{PF}_6^{-}, \text{AsF}_6^{-}, \text{SbF}_6^{-}, \text{NO}_3^{-}, \text{CF}_3\text{SO}_3^{-}\), tosylate). The \(\beta\)-diketonato ligand (\(\text{Hbppd}\), see Scheme 1), besides acting as a chelating agent on the Fe\(^{III}\) center, can donate the 4-pyridyl groups to external metals. The \([\text{Fe}^{II}(\text{bppd})_3]\) metallo ligand has thus six exo-donor groups with an approximate octahedral orientation. In the networking process a variable number of pyridyl donors are employed, \textit{i.e.} four, five and six, giving frameworks of increasing complexity and dimensionality, that have been structurally characterized (see Table 1); the dependence of the framework structures on the counter-anions has been investigated. This bppd ligand seems to be particularly suitable in the preparation of chelate metalloligands for the engineering of heterometallic networks but in spite of this, curiously, it has been used only very recently in this concern: the complex \([\text{Gd}(\text{bppd})_3](\text{H}_2\text{O})\) that forms a 1D linear chain structure has been described in 2009 and, during the preparation of this paper, a communication has appeared reporting the Group 13 metallo ligand \([\text{Al}(\text{bppd})_3]\) (\(\text{M} = \text{Al}^{III}\) or \(\text{Ga}^{III}\)) together with the mixed-metal frameworks obtained by reaction with silver salts. We describe here also the reactions of \([\text{Al}(\text{bppd})_3]\) with the same Ag\(X\) salts employed with the analogous Fe(III) metallo ligand.

**Experimental procedures**

**General procedures**

All the commercial reagents and solvents employed (Sigma-Aldrich) were of high-grade purity and used as supplied, without further purification. All manipulations were performed under aerobic conditions unless standard Schlenk techniques were required. Anhydrous tetrahydrofuran was freshly distilled under nitrogen from sodium/benzophenone. NMR spectra were recorded on Bruker AC300 or AC400 instruments; \(\delta\) values are given in ppm relative to tetramethylsilane. Infrared spectra were collected on a Perkin-Elmer Paragon 1000 FT-IR spectrometer equipped with an \(i\)-series FT-IR microscope. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 instrument under dynamic nitrogen flow (20 cm\(^3\) min\(^{-1}\)). A ramp rate of 10 °C min\(^{-1}\) in the temperature range 20–700 °C was used. The purity of all synthesized compounds was checked by X-ray powder diffraction analyses. Powder patterns were recorded on a Philips PW1820 diffractometer (Cu K\(\alpha\) radiation, \(\lambda = 1.5405\) Å), in the 5–35° 2\(\theta\) range (0.02° and 2.5 s per step). Magnetic susceptibilities (\(\chi_M\)) were determined at room temperature using a MSB-AUTO (Sherwood Scientific Ltd.) magnetic balance. Three measurements for every sample (50–100 mg) were performed. Diamagnetic corrections were estimated from Pascal’s constants.

**Synthesis**

1,3-Bis(4-pyridyl)-1,3-propanedione (\(\text{Hbppd}\)). 4-Acetylpyridine (3.0042 g, 24.80 mmol) was added under nitrogen to NaH (60% dispersion in mineral oil, 2.0075 g, 50.1 mmol) and anhydrous THF (7 mL). A solution of ethyl isonicotinate (7.5007 g, 49.6 mmol) in THF (8 mL) was then added dropwise in about 20 min under continuous stirring (exothermic reaction). The mixture was heated at 65 °C for 1 h and 40 minutes under nitrogen flux. After quenching, by addition of iced water (about 40 mL), the pH was adjusted to neutrality with glacial acetic acid. From the neutral mixture the ligand \(\text{Hbppd}\) precipitated as a whitish solid, which was recovered by filtration, washed with water and dried in air (yield 71%). IR (KBr) \(\nu_{\text{max(cm}^{-1}\text{)}}\): 3548w, 3482w, 3414m, 2922m, 2874m, 1616vs, 1586vs, 1546vs, 1492vs, 1460s, 1385s, 1274m, 1238s, 1214s, 1056s, 992m, 936w, 902w, 844m, 786s, 704m, 684m, 606s, 494m, 466m. \(^1\)H NMR (300 MHz, acetone-

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<th>No.</th>
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<th>Structural motifs</th>
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<td>([\text{Fe}(\text{bppd})_3]): xSolv</td>
<td>Tris-chelate metallo ligand</td>
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<td>2a–e</td>
<td>([\text{Fe}(\text{bppd})_3\text{Ag}(X)])</td>
<td>2D (4,4) sq1, undulated layers</td>
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<td>3a</td>
<td>([\text{Fe}(\text{bppd})_3\text{Ag}(\text{CF}_3\text{SO}_3)])</td>
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<td>4</td>
<td>([\text{Fe}(\text{bppd})_3\text{Ag}_2(\text{NO}_3)])</td>
<td>3D 4,5-connected, 2-fold interpenetrated</td>
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<td>5a</td>
<td>([\text{Fe}(\text{bppd})_3\text{Ag}_2(\text{tosylate})])</td>
<td>3D single trinodal net, 3,4,6-connected</td>
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</table>

**Table 1** List of the products and their structural type
THF and dried in air. Yield 66.7%. 

Tris[1,3-bis(4-pyridyl)-1,3-propanedionato]aluminium(n)(1b). Compound 1b was obtained as a microcrystalline white powder following the procedure described for 1a using AlCl₃ as a source of aluminium. Yield 99%. IR (KBr) v_max/cm⁻¹ 3041m, 2945s, 1487vs, 1385s, 1319s, 1302vs, 1278s, 1259s, 1125s, 1062s, 1031s, 945m, 850s, 785s, 718m, 697s, 664w, 638s, 622s, 541m, 476m.

[Fe₃⁺(bppd)₅AgX·4THF (X = BF₄⁻, ClO₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻)] (2a–e). Compounds 2a–e were obtained by similar procedures using the proper silver salt. The synthesis of 2c is described here as a representative example: a CH₃CN solution of AgCF₃SO₃ and THF solution of 1a (0.101 mg, 0.137 mmol) dissolved in THF (10 mL). On leaving the mixture under stirring for 16 h a red solid was collected on a Buchner funnel by filtration, washed with THF and dried in air. Yield 66.7%. IR (KBr) v_max/cm⁻¹ 3650m, 3460b, 3112m, 3043m, 2920m, 1756vs, 1520s, 1449s, 1359s, 1304s, 1223m, 1080s, 1061s, 946m, 880s, 831s, 794s, 719s, 702s, 623s, 557s, 477s.

Compound 2a: yield 27.3%. IR (KBr) v_max/cm⁻¹ 3103m, 3043m, 1579s, 1528s, 1486s, 1421s, 1385s, 1318s, 1302s, 1223s, 1060s, 944m, 849m, 784s, 718m, 698s, 622s.

Compound 2b: yield 76.3%. IR (KBr) v_max/cm⁻¹ 3384b, 3104m, 3046m, 1576s, 1520s, 1486s, 1418s, 1362s, 1318s, 1302s, 1223m, 1099s, 1061s, 944m, 849m, 785s, 718m, 698s, 623s, 543s, 476s.

Compound 2d: yield 68.8%. IR (KBr) v_max/cm⁻¹ 3368b, 3116m, 3044m, 1579s, 1523s, 1486s, 1420s, 1385s, 1367s, 1318s, 1302s, 1223m, 1078w, 1062s, 1002w, 945m, 850s, 786m, 700s, 622s, 542m, 476m.

Compound 2e: yield 71.6%. IR (KBr) v_max/cm⁻¹ 3417b, 3111m, 3047m, 2975m, 2929w, 1576s, 1528s, 1487s, 1421s, 1387s, 1318s, 1304s, 1223m, 1062s, 945m, 851m, 793m, 718s, 700m, 659s, 623s, 546m, 477m.

Crystals of 2a–e suitable for X-ray analyses were obtained by slow diffusion of 9 × 10⁻⁴ M ethanolic solution (4 mL) of 1a into a 1.8 × 10⁻¹ M aqueous solution (4 mL) of AgCF₃SO₃ in about 10 days.

[Fe₃⁺(bppd)₅Ag(II)(NO₃)₆] (4). A solution of AgNO₃ (19.3 mg, 0.114 mmol) in H₂O (10 mL) was slowly added (in about 10 min) to a solution of 1a (54.2 mg, 0.0741 mmol) dissolved in EtOH (10 mL). The mixture was left under stirring for 16 h. The red solid was collected on a Buchner funnel by filtration, washed with EtOH and dried in air in order to obtain pure 4 (yield 81%). Samples of compound 4, showing lower crystallinity, have also been obtained using CH₃CN solution of AgCF₃SO₃ and THF solution of 1a (yield 83%). IR (KBr) v_max/cm⁻¹ 3418b, 3111, 3044m, 1578s, 1523s, 1486s, 1420s, 1384s, 1364s, 1318s, 1303s, 1223s, 1062s, 944m, 849m, 785s, 718m, 698m, 664w, 622s, 543s, 477m.

Crystals of 4 suitable for X-ray analysis were obtained by slow diffusion of a 9 × 10⁻⁴ M ethanolic solution of 1a into a 2.7 × 10⁻³ M aqueous solution of AgNO₃ (4 mL) in about 10 days.

[M₃(bppd)₅Ag₅(I)(tosylate)] [M = Fe(II) (5a), Al(II) (5b)]. Compounds 5a and 5b were obtained by similar procedures on reacting respectively 1a and 1b with silver tosylate. Only the synthesis of 5a is described here in detail. A solution of Ag tosylate (62.7 mg, 0.2246 mmol) in CH₃CN (10 mL) was slowly added (in about 30 min) through a drop funnel to a solution of compound 1a (98.3 mg, 0.1344 mmol) dissolved in THF (10 mL). The mixture was left under stirring for 22 h to allow the complete precipitation of 5a as a red solid. The red solid was collected on a Buchner funnel by filtration, washed with EtOH and dried in air to give pure 5a (yield 30.7%). IR (KBr) v_max/cm⁻¹ 3421b, 3041m, 2920m, 1578s, 1519s, 1486s, 1418s, 1384s, 1364s, 1318s, 1302s, 1216s, 1191s, 1126s, 1062s, 1037s, 1012s, 944m, 848s, 784s, 718m, 696s, 665w, 621s, 569s, 541m, 476m.

Compound 5b: polycrystalline product: yield 98%. IR (KBr) v_max/cm⁻¹ 3421b, 3039w, 2919w, 1590s, 1534s, 1487s, 1439s, 1420s, 1387s, 1313m, 1312s, 1211s, 1191s, 1129s, 1064m, 1042m, 1013m, 951m, 850w, 815w, 783m, 722m, 666w, 692s, 633m, 570m, 560sh, 534m, 483m, 423m.

Red hexagonal prismatic crystals of 5a suitable for X-ray analysis were obtained by slow diffusion of a 8 × 10⁻⁴ M THF solution of 1a into a 2.4 × 10⁻³ M CH₃CN solution of Ag tosylate (4 mL) in about 4 days.
Transformation of 3 to 4. Procedure A: 7.9 mg (0.007 mmol) of ground crystals of 3a were added to a solution of AgNO₃ (1.6 mg, 0.009 mmol) and NaNO₃ (1.3 mg, 0.015 mmol) in EtOH/water (1 : 1) (4 mL). The mixture was left to stand for 15 days at room temperature. The red solid was then collected on a Hirsch funnel by filtration, washed with EtOH and dried in air to give pure 4x (6.5 mg).

Procedure B: 13.3 mg (0.004 mmol) of ground crystals of 3a were added to a solution of AgNO₃ (2.5 mg, 0.015 mmol) in EtOH/water (1 : 1) (4 mL). The mixture was left to stand for 15 days at room temperature. Then the red solid was collected on a Hirsch funnel by filtration, washed with EtOH and dried in air to give pure 4y (12.7 mg).

Thermogravimetric analyses (TGA)

The analyses were performed on compounds 1a, 2a–d, 3a, 4 and 5a. They show a weight loss of about 5% in the range 20–160 °C (1a), 2–3% in the range 20–100 °C (2a, 2b), 5% in the range 20–170 °C (2c, 2d), 5% in the range 20–70 °C (3a, 4), 5% in the range 20–110 °(5a) due to de-solvation processes. Compound 1a is stable up to 250 °C, while network decomposition of 2a, 2b, 3a, 4 and 5a starts at different temperatures depending on the nature of the polymers (range 200–230 °C).

Crystallography

Data were collected on a Bruker APEXII-CCD diffractometer using MoKα radiation (λ = 0.71073 Å). Empirical absorption corrections (SADABS) were applied to all data. The structures were solved by direct methods (SIR97) and refined by full-matrix least squares on F² (SHELX-97) using the WINGX interface. All hydrogen atoms were placed in geometrically calculated positions and subsequently refined using a riding model with Uiso(H) = 1.2 Ueq(C) (Table 2). The accessible free voids were calculated by PLATON. Full details of the refinements can be found in the cif file (under refine_special_details keyword). Crystals of all monomers and polymers are unstable in air and were kept under mineral oil and collected at low temperature (150 K for all but 120 K for 5a). Compound 1a was collected at room temperature and any attempt to find other crystals to re-collect it at low temperature was unsuccessful. All tested crystals of 1a, 2a, 3a, 4 and 5a also showed weak diffraction, hence resulting in high R values. Excluding 3a and 5a, anisotropic thermal parameters were assigned to all non-hydrogen atoms, except for clathrate THF molecules (in 2a, 2b), disordered anions or parts of ligands (in 2a, 2c, 4). In the extreme cases of compounds 3a and 5a, due to the poor diffraction (and a strong decay of 31% for 3) of all the sampled crystals, only the heaviest atoms were refined with anisotropic thermal parameters, so as to allow a reasonable parameter/observation ratio and result in an acceptable structural model. For the same reason some groups were refined as rigid body: the anions in 2a, 2b and one trilate in 3a. Furthermore all structures of 1a, 3a, 4 and 5a were found to contain disordered solvants (such as tetrahydrofuran, ethanol, acetonitrile and water). Since it was difficult to refine a consistent model for the solvents, their contribution was subtracted from the observed structure factors according to the BYPASS procedure, as implemented in PLATON with the command SQUEEZE. Topological analyses were performed with TOPOS.

Results and discussion

The [Fe(bppd)₃] metalloigand

The synthesis of 1,3-bis(4-pyridyl)-1,3-propanedione (Hbppd) was carried out according to a literature method, using a base-catalyzed condensation between 4-acetylpyridine and ethyl isonicotinate.

The tris-chelate [Fe(bppd)](1a) metalloigand was obtained in good yields by mixing water solutions of Hbppd, NaOH and FeCl₃·6H₂O under stirring for 3 h. Slow evaporation of a THF solution of the crude bulk product afforded red needle-like crystals suitable for X-ray analysis, of formula [Fe(bppd)]xSolv (1a’). The structure of 1a’ has been determined by X-ray diffraction since it seemed to be a potentially useful chiral building block for networking. Moreover, magnetic measurements at RT show that it is a high-spin d⁵ species that can be used to introduce magnetic centers in a polymeric network.

The crystal structure of 1a’ consists of chiral tris-chelate complexes with rather distorted octahedral geometry around the metal center. The asymmetric unit comprises an entire complex in a general position [complex A, containing Fe(1)], and another half one [complex B, containing Fe(2)], with the metal atom placed in a special position on a 2-fold axis (Wyckoff c position). Complexes A and B are chemically equivalent but crystallographically distinct. Two adjacent independent complexes, A and B, exhibiting opposite conformation (Δ and Δ), are shown in Fig. 1.

The coordination polyhedra of both complexes are similar, with an irregular octahedral geometry. The Fe–O bond lengths are in the range 1.945(8)–2.007(6) Å for Fe(1) and 1.975(5)–2.019 (6) Å for Fe(2), and the bite angles O–Fe–O are in the ranges 87.2 (3)–87.4(3)° [with Fe(1)] and 86.1(2)–87.2(3)° [with Fe(2)].

The FeO₂C₃ chelate rings show some deviations from planarity. This can be quantified by the angle between the FeO₂C₃ chelate rings [range 1.7(5)–49.7(7)°]. The coordination of the pyridyl groups to the planes of their chelate rings [range 1.7(5)–49.7(7)°].

An intriguing feature of this structure is the packing of the discrete complexes that leaves large free voids corresponding to 22.6% (0.19 cm³ g⁻¹) of the cell volume. A crystallographic cell contains 12 complexes, 8 of type A (4A + 4A), and 4 of type B (2A₂B + 2A₂).

Complexes A form 2D layers that stack along a alternating with 1D chains running in the c direction that contain only complexes B (as illustrated in Fig. 2). The voids are located in the parallel channels running along c.
By reacting Hbppd and AlCl$_3$ under the same conditions used to obtain 1a, it was also possible to obtain the aluminium derivative [Al(bppd)$_3$] (1b). Compound 1b was isolated in good yields as white microcrystalline powder and characterized by IR, $^1$H NMR spectroscopy and XRPD. The X-ray powder diffraction patterns of 1a and 1b are comparable with one another but different from the pattern calculated from the structure of 1a (see Fig. S1 and S2†).

Table 2 Crystallographic data

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Fig. 1 The two adjacent independent tris-chelate complexes in compound 1a [complex $A$, containing Fe(1), and complex $B$, containing Fe(2)] that show opposite conformation ($\Lambda$ and $\Delta$). Complex $B$ is located on a 2-fold crystallographic axis. # Symmetry code: 2 $-x$, $y$, $\frac{1}{2} - z$.

Fig. 2 View of the packing down c in 1a (top) showing the stacking (along a) of layers of complexes $A$ (red) alternating with coplanar parallel chains of complexes $B$ (blue). The two types of sheets are illustrated below, with different shadings that evidence the opposite conformations ($\Lambda$ and $\Delta$) of the complexes.
The heterometallic coordination networks

Complex 1 is a suitable neutral metalloligand exhibiting six exo-oriented donor pyridyl groups that can, in principle, work as a 6-connected node in the building of heterometallic metal-organic frameworks. Paralleling our recent work based on similar tris-chelate metalloligands, [MIII L3] [M = FeIII and CoII] and [MIII L3] [M = MnII, CoII, ZnII, CdII] with HL = 1,3-bis(4-cyano-phenyl)-1,3-propanedione, we have reacted 1 with many AgX salts. While the above [MIII L3] and [MIII L3] species afforded in all cases the same type of 3D structure (6-fold interpenetrated Pcu topology) that crystallizes in the same space group with similar cell parameters, in spite of the different metal ions, ionic charges and X- silver counter-anions, in the present work we observe that with [Fe(bppd)3] the outcoming MOFs are varied and strongly dependent on the type of AgX salt employed. We have obtained four different types of heterometallic polymeric frameworks, i.e. a family of five isomorphous 2D single-sheet species (compounds 2a–e) when X- are pseudo-spherical anions (tetrahedral or octahedral) of poor coordinating ability, a 2D double-layered species (compound 3a) with silver trflate, a 3D 2-fold interpenetrated complex network (compound 4) with silver nitrate and a single 2D nanoperpored network (compound 5a) with silver tosylate (see Table 1). This structural sequence illustrates also a progressive increase of the pyridyl groups of the metalloligands that act as donors. Indeed, though the building blocks are in principle able to work as six donors, we observe here cases in which a lower dionicity is present (four or five donor groups employed) in all species but in compound 5. The metalloligands contained as building blocks in the heterometallic coordination networks maintain essentially the same structure as in the free species.

The family [Fe(bppd)3Ag](X)-4THF [X = BF4-, ClO4-, PF6-, AsF6-, SbF6- (2a–e)]

The reactions of 1 in THF with AgX salts (X- = BF4-, ClO4-, PF6-, AsF6-, SbF6-) in acetonitrile produce the family 2a–e. Single crystals were obtained for all these species, showing that they are isomorphous, but complete X-ray analyses were carried out only for 2a–c, while the other two species gave crystals of poorer quality and they were simply characterized by their cells, exhibiting very similar parameters by single-crystal X-ray diffraction. The general formulation is [Fe(bppd)3Ag](X)-4THF; the structure with X- = PF6- (2e) is described here, as representative of the whole family.

The crystal structure of these species consists of 2D undulated layers of 4*-sq14*- topology, showing the alternation of metalloligands and silver ions as 4-connected nodes. All the metalloligands are located in a special position on 2-fold axes and use the two pyridyl groups of one bppd ligand and one pyridyl group for each of the other two ligands to bind to silver metals (see Fig. 3). Two cisoid pyridyl groups remain dangling so that the node geometry can be described as of the saw-horse type.

The silver nodes, also lying on 2-fold axes, are distorted tetrahedral, being bound to four N-pyridylic atoms with Ag–N bond lengths of 2.284(4) and 2.332(4) A and bond angles in the range 98.5(2)–126.3(2)°. These two types of nodes produce the undulated 2D layers, illustrated in Fig. 4. In these layers the 4-gon windows are 28-membered rings. These large rings can be idealized to rhombuses with Fe–Ag edges of 9.110(2) and 9.270(2) A. There are two kinds of rhombuses [Fe–Ag–Ag–Ag] for each of the silver edges: 14.545(3) vs. 13.410(3) and Ag–Ag–Ag; 11.238(3) vs. 12.571(3) that are alternately disposed, as a chessboard, with the anions located in the more distorted windows (see Fig. 5).

Within each layer the metalloligands in the ’upper’ rows (crests) are all homochiral and of opposite chirality with respect to those in the ’lower’ rows (valleys).

The layers have a certain thickness (18.67 A, from the top and the bottom planes of the N atoms of the uncoordinated pyridyl groups) and stack with an ABAB sequence down b (see Fig. 6) with great interdigitation (overlap thickness of 4.83 A).

The anions occupy intralayer spaces i.e. are placed at the centers of alternate rhombic cavities (positions corresponding to inversion centers). Four pyridyl groups are present in the edges of the rhombuses, two (opposite) with their rings in the plane of the window and two (opposite) with their rings almost perpendicular (see Fig. 7). These cavities are particularly suited for the encapsulation of octahedral anions such as PF6-, AsF6- and SbF6- (as well as disordered tetrahedral ones such as BF4-, ClO4-, with a sort of pseudo-octahedral shape) because of significant σ-anion (i.e. H-bonds) and π-anion interactions. Ab initio theoretical calculations have recently shown that the anion-binding properties of pyridine and pyrazine are dramatically enhanced by their coordination to silver ions. The presence of the coordinated metal increments both the π and the σ anion-binding ability. Detailed values of these interactions for the PF6-, AsF6- and SbF6- species are reported in the ESL†. The presence of the anions in all 2a–e compounds was confirmed by IR spectroscopy.

The THF molecules are placed in the interlayer spaces, near to the more regular windows. The percentage of free void calculated...
with the program PLATON after the removal of clathrate THF molecules is 39.7% of the cell volume for 2c.

Thermal gravimetric analyses, performed on compounds 2a–d, show that almost all the THF molecules are lost at room temperature. The remainder (2–5%) is lost in the ranges 20–100 °C for 2a,b (tetrahedral anions) and 20–170 °C for 2c, d (octahedral anions). The networks decomposition starts at different temperatures depending on the polymers (range 200–230 °C).

The double-layered [Fe(bppd)3Ag](CF3SO3) (3a)

The structure of [Fe(bppd)3Ag](CF3SO3) (3a), which exhibits the same framework composition of the previous family 2, shows a completely different type of [Fe(bppd)3Ag]+ 2D polymeric frame, probably due to the variation in shape and chemical behaviour of the anion that consists of a double layer, comprised of two superimposed honeycomb-like sheets of $6^2$-hcb7 topology. The metalloligands again employ only four out of the six pyridyl donor groups for networking (see Fig. 8). The three bppd ligands, however, play different roles, i.e. in detail: the first ligand uses both its pyridyl groups to bind two Ag atoms in one layer, the second ligand uses only one pyridyl group to bind the third Ag atom in the same layer, with the other pyridyl group dangling outwards in the direction normal to the layer, while the third ligand works as a bridge that joins the two layers, with one pyridyl group that binds an Ag atom of the second layer and with the remaining pyridyl group that is dangling in the plane of the first layer.

There are two independent metalloligands [containing Fe(1) and Fe(2), respectively] and two independent silver atoms. The first metalloligand exhibits Fe(1)–O bond distances in the range 1.880(11)–2.029(8) Å and bite angles O–Fe(1)–O in the range 85.5(3)–86.6(4)°. All the three metallocycles are markedly distorted from planarity, with O2C3/FeO2 angles in the range

Fig. 5 Top views (down b) of the 2D layer of compound 2c: (top) molecular drawing illustrating the presence of two types of windows alternately disposed, as in a chessboard, and (bottom) a schematic drawing with rhombuses having two kinds of vertexes (Fe and Ag, evidenced by different colors). The disposition of the anions (blue) and the guest THF molecules (green) is also shown.

Fig. 6 Stacking of the layers in 2c.

Fig. 7 View of a rhombic cavity containing PF6− in a layer of 2c. The interactions of the pyridyl groups on the walls with the anions are discussed in the text.

Fig. 8 The geometry of the metalloligand in 3a with only four of the six pyridyl groups bound to ‘tetrahedral’ Ag ions.
18.9(5)–24.3(5)°. The pyridine rings are significantly rotated with respect to the plane of the three central carbon atoms, with values in the large range 12.1(4)–38.7(5)°. Within the other metallogenoligand the Fe(2)–O bond lengths span the interval 1.955(8)–2.087(9) Å and the bite angles O–Fe(2)–O span the interval 87.3(3)–90.6(3)°. The three metallocycles are even more deviating from planarity, with dihedral angles in the range 17.5(3)–27.4(8)°. Again the pyridine rings are strongly rotated with respect to the central carbon atoms plane, with the value in the large range 9.5(5)–37.1(8)°.

The distorted tetrahedral silver atoms exhibit the following bond parameters: Ag(1)–N 2.286(6)–2.313(8) Å and N–Ag(1)–N 97.4(3)–124.9(3)°, Ag(2)–N 2.296(6)–2.363(8) Å and N–Ag(2)–N 87.6(3)–125.9(3)°. Though the structural characterization has been performed at 150 K, one coordinated pyridine ring is disordered with two positions, with an occupancy of 63% and 37%.

The polymeric frame is a thick double layer (distance between the planes containing the metalloligands in the two layers of 10.35 Å), formed by two superimposed $6^3$-$hcb^7$ sheets. Within each sheet the 6-gons are comprised of alternating three metalloligands and three silver atoms. The silver nodes are 4-connected (bound to three pyridyl groups of the same layer and to one group from the other layer). A schematic view of the double layer is shown in Fig. 9. The two sheets are staggered in such a way that the silver atoms of the upper one correspond to the iron metalloligands of the lower one (and vice versa). The topology is that of an uninodal 2D network of point symbol $4^3.6^6$; a previous example of double layer with this topology is $[\text{RuCl}_2(\text{pyz})_2\text{Ag}(\text{SO}_3\text{CF}_3)]_n$. The network edge dimensions are Fe–Ag 9.049(4), 9.074(2), 9.120(2) Å and 9.061(2), 9.123(2), 9.139(3) Å (intralayer) and Fe–Ag 9.218(4) and 9.123(2) Å (interlayer) (many details are reported in the ESI†).

Two views of the framework (side and top) are illustrated in Fig. 10. As can be observed, there are some notable structural features: (i) dangling pyridyl groups protrude outside the double layer on both sides, which play an important role in the stacking of these 2D motifs (see below); (ii) the framework contains cages of idealized hexagonal prismatic shape that are occupied by the triflate anions; (iii) remarkably all the metalloligands of an individual double layer are homochiral ($\Delta$ or $\Lambda$), while the adjacent double layers (upper and lower) show opposite chirality.

The double layers are parallel to the $ab$ crystallographic plane and stack in the normal direction ($c^*$) with the lateral shift, as shown in Fig. 11.

The dangling pyridyl groups on both sides of each double layer are threaded into the 6-gon meshes of the two adjacent (upper and lower) double layers, resulting in an extended polythreaded array. The polythreading is favoured by $\pi$–$\pi$ interactions that involve the dangling pyridyl rings of adjacent double layers (centroid–centroid distance of 3.690 Å).

The theoretical free space of this polymer is about 21.1% of the cell volume.

The XRPD pattern of the bulk product shows a limited crystallinity, but confirms that the structure is retained by comparison with the calculated pattern. The presence of triflate anions was confirmed by IR spectroscopy.
The TGA of 3a showed a first weight loss of 2.3% in the range 20–185 °C, due to desolvation, and a second weight loss of 57.5% starting at ca. 200 °C due to network decomposition.

Polycrystalline samples of the aluminium derivative [Al(bppd)2Ag](CF3SO3) (3b) were obtained after reacting the metalloligand 1b with silver triflate under experimental conditions similar to those used to synthesize 3a. The nature of 3b was assessed comparing its XRPD patterns with that of 3a.

The 3D interpenetrated species [Fe2(bppd)6Ag3(NO3)3] (4)

When silver nitrate and silver tosylate are used the anions interact with the silver atoms and this results in the formation of 3D polymers, namely [Fe2(bppd)6Ag3(NO3)3] (4) and [Fe(bppd)2Ag]3(tosylate)5 (5a).

The network of [Fe2(bppd)6Ag3(NO3)3] is strictly related to the above described 2D structure of compound 3a [Fe(bppd)2Ag] (CF3SO3). In this 3D network the same double layer of the 2D 3D polymers, interact with the silver atoms and this results in the formation of a derived binodal net with the name fsx-4,5-R3m.19

The silver atoms that work as spacers [Ag–N 2.114(13), 2.075(13) Å, N–Ag–N 163.3(5)°] lie close to inversion centres (being therefore statistically disordered on two adjacent positions); they bear in addition a terminal weakly bonded nitrate [Ag–O(NO3)2 2.631(13) Å] and are inserted inside the cages of the double layers (see above) belonging to the second interpenetrated network. In other words, starting from the structure of compound 3a, these silver atoms find their location approximately in the midpoint between each pair of pyridyl groups threading the double layers by opposite directions [the (py)N⋯N (py) nonbonding contact passes from 3.43(2) Å in 3a to 4.14(2) Å in 4] (see Fig. 13).

The chirality pattern of the metalloligands observed in 3a (alternation of ‘all Λ’ double layers with ‘all Δ’ double layers) is maintained in 4; thus the additional Ag spacers form two 3D nets of opposite chirality (a crystalline racemate).

It is worth noting that the previously reported reactions of the strictly related metalloligands [M(bppd)3] (M = AlIII or GaII) with AgNO3 afford a quite different and more usual coordination polymer, i.e. a 3-fold interpenetrated pcu network.20

TGA of compound 4 showed a weight loss of about 2% in the 20–130 °C range due to desolvation and a second weight loss of about 62.6%, starting at 150 °C, due to network decomposition.

The structural correlation observed between compounds 3a and 4 has prompted us to attempt to transform the former one into the second by reacting powder samples of 3a with a solution of silver nitrate. The transformation has been monitored by XRPD and IR spectroscopy (see Fig. S7 and S8†). The results show that the final product presents a powder diffraction pattern very similar to that of 4 but the IR spectrum reveals the presence of both anions (triflate and nitrate), i.e. the triflate anions have not been completely displaced and the compound is a mixed salt, isomorphous with 4.

The 3D nanoporous [Fe3(bppd)9Ag5(tosylate)5] (5a)

The reaction of 1 with silver tosylate produces a complex 3D nanoporous network, [Fe3(bppd)9Ag5(tosylate)5] (5a), exhibiting 6-connected metalloligands and 3- and 4-connected silver ions. It is worth noting that it is the unique network within these heterometallic Fe/Ag species in which 1 uses all the six pyridyl donor groups.

This metalloligand was just intended as an octahedral 6-connected building block for the engineering of networks, and such a behaviour has been previously observed with strictly similar metalloligands,8,10 that, by reactions with silver salts, generate frameworks showing the 6-e pcu™ topology. At difference, the...
single 3D network of 5a exhibits a novel trinodal topology, with 3-connected (3-c, Ag), 4-connected (4-c, Ag) and 6-connected (6-c, Fe) nodes in the ratio 2 : 3 : 3, i.e. with the \([3-c]_2[4-c]_3[6-c]_3\) stoichiometry and point symbol \((6')_3(4',6')_3(4',6',8')_3\).

Within the metalloligand the Fe–O bond distances are in the range 1.931(7)–1.993(8) Å and the O–Fe–O bite angles are in the range 87.6(3)–88.5(4)°, similar to the values in 1a. One metal-local cycle is very close to planarity (dihedral angle of 0.4(5)°) while the other two equivalent show a large deviation (dihedral angle of 28.1(7)°). Also in this case the pyridine rings are strongly rotated with respect to the plane of the three central carbon atoms (range 3.8(6)–35.2(6)°).

An interesting rationalization of this novel network is the following one: large 1D parallel metal–organic nanotubular motifs of hexagonal section can be envisaged, all running in the c axis direction, with square-meshed walls that are laterally interconnected by additional Ag triple-bridging atoms to generate the whole 3D array.

A single nanotube is illustrated in Fig. 14; its stoichiometry is \([\text{Fe}(\text{bppd})_3\text{Ag}]^+\), like that of the previously described 2D species 2 and 3a. It can be conceptually considered as a rolled version of a single 4+-sq layer of compounds 2 (obviously in this case with the dangling pyridyl groups all oriented on the same side, i.e. outwards the tube), with the walls of the tube formed by the same type of square meshes as in 2. Independent metal–organic nanotubes, held together by alkaline cations, with a similar topology have been recently described,\(^{20}\) based on Cd\(^{2+}\) ions and the bent ligand 4-amino-3-[(pyridin-4-ylmethylene)amino] benzoate. From a theoretical point of view, the curling-up or rolling-up mechanism of topological transformation from 2D sheets to 1D tubes is illustrated by the structural comparison of a single 2D layer of 2 with a nanotube of 5a. It is worth noting that like the rolling-up of graphite to single walled carbon nanotubes can be ideally carried out in different ways, also within metal–organic nanotubes, the parent 4+-sq layers can be rolled in such a way to dispose along the tube axis either the 4-gon diagonals, as in the Cd species previously cited,\(^{20}\) or the 4-gon edges as in 5a.

Another interesting structural similarity can be envisaged: the nanotubes originate from the superposition of hexagonal rings similar to those of the honeycomb-like layers of 3a, constituted by alternating three silver atoms and three metalloligands. The superposition of the rings occurs in a staggered fashion, like in 3a. The three metalloligands in a ring are homochiral while those of the two adjacent rings (upper and lower) show opposite conformation. A nanotube is therefore a \(\Delta\Delta\Delta\Delta\ldots\) sequence of rings.

These tubular motifs are connected among them via the two remaining pyridyl groups of each metalloligand that are coordinated to 3-connected silver atoms. These 3-connected silver atoms have the function to link and space out the tubes three by three (see Fig. 15 and 16). These Ag nodes lie on 3-fold axes and exhibit a pyramidal geometry, being bound to three pyridyl nitrogen atoms [Ag–N 2.27(1) Å and N–Ag–N 113.4(5)°] and weakly interacting with a (disordered) tosylate anion [Ag–O 2.275(13) Å]. Though the X-ray data collection has been performed at 120 K, the anion is strongly disordered on three positions, with an occupancy of 33%.

The network presents high theoretical porosity of about 50% of the unit cell volume; the voids are mainly distributed in the large hexagonal channels (i.e. in the single walled metal–organic nanotubes, Fig. 16).

The XRPD pattern of the bulk product 5a shows a different crystalline structure when compared with the pattern calculated from single crystal. On the other hand, it is comparable with the powder pattern of ground single crystals. A possible explanation is that the structure of 5a, probably due to the loss of guest solvents, rearranges to a different uncharacterised species. The presence of the anions was confirmed by IR spectroscopy.

**Fig. 15** View of the nanoporous network in compound 5a.

**Fig. 14** Molecular (top) and schematic (bottom) front and side views of a nanotube in 5a. The orange spheres represent Fe atoms and the pink spheres represent Ag atoms.

**Fig. 16** Schematic view of the network in 5 evidencing the nanotubes (in red).
TGA of compound 5a showed a weight loss of about 4.9% in the 20–120 °C range due to desolvation and a second weight loss, starting at 250 °C, of about 47.6% corresponding to network decomposition.

The aluminium derivative [Al3(bppd)9Ag5(tosylate)5] (5b) was also obtained as a polycrystalline material. The nature of 5b was confirmed by comparison of its XRPD powder pattern with that obtained by grinding crystals of 5a.

Conclusions

In this paper we have investigated the use of the novel metalloidligand [Fe(bppd)]3 (1a) as well as the aluminium analogue for the construction of heterometallic networks with reactions with silver salts. This well-established synthetic strategy, involving the use of rigid building blocks with exo-donor groups, can sometimes result in structural motifs different from the target structure because not all the potential donor groups are used in the networking process. The results reported here, at difference from what was observed in other studies involving similar tris-chelate octahedral complexes with six exo-oriented donor groups,8,10 show that 1a can employ four, five or six pyridyl donors to give a variety of heterometallic networks depending on the nature of the silver counter anion. We have obtained a family of 2D 4\(^2\)-sql networks with undulated single layers of rhomnic meshes that contain anions that are pseudo-spherical [e.g. BF\(_4\), ClO\(_4\), PF\(_6\), AsF\(_6\), SbF\(_6\) (2a–e)]. In these species the metalloidligands use only five of the donor pyridyl groups. The same occurs in compound 1a by reaction of AgNO\(_3\). Finally, the structure of 5a was confirmed by comparison of its XRPD powder pattern with that obtained by grinding crystals of 5a.

Acknowledgements

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