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ARTICLE

## Discrete and polymeric complexes formed from cobalt(II), 4,4'-bipyridine and 2-sulfoterephthalate: synthetic, crystallographic and magnetic studies

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A series of five coordination compounds, namely,  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Co}_2(\text{stp})_2(\text{bipy})_5(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}\}_n$  (**2**),  $[\text{Co}_3(\text{stp})_2(\text{bipy})_4(\text{H}_2\text{O})_{10}]\cdot 8\text{H}_2\text{O}$  (**3**),  $[\text{Co}(\text{Hstp})_2(\text{Hbipy})_2]$  (**4**) and  $\{[\text{Co}(\text{stp})_2(\text{H}_2\text{O})_2][\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]\cdot 2\text{Hbipy}\cdot 2\text{H}_2\text{O}$  (**5**) have been synthesised hydrothermally, through the reaction of different molar ratios of 2-sulfoterephthalic acid monosodium salt,  $\text{Na}(\text{H}_2\text{stp})$ , cobalt(II) nitrate hexahydrate and the N-donor ancillary co-ligand 4,4'-bipyridine (bipy). Due to the combination of the multiple potential coordination modes of the **stp** ligand and the bipy co-ligand, the products are structurally and topologically diverse with the connectivities of the materials dependent on the ratios of starting materials employed. Single-crystal X-ray diffraction studies show that compound **1** is a three-dimensional coordination polymer, compound **2** consists of infinite one-dimensional zig-zag chains, compound **3** is a discrete trinuclear complex, compound **4** is a discrete mononuclear complex and compound **5** is an ionic solid consisting of both cobalt containing cations and anions. Magnetic studies show that the Co(II) ions in **1** are strongly coupled, while **2**, **3** and **5** show insignificant coupling due to larger metal-metal separations. Modelling required the introduction of zero field splitting parameters due to orbital angular momentum contributions in these cases.

### Introduction

Over the last twenty years, there has been a growing interest in the use of relatively simple chemical building blocks to construct topologically complex molecules, whether they are discrete (including interlocked architectures, links, knots and ravel) or polymeric (including coordination polymers and metal-organic frameworks).<sup>1, 2, 3-5</sup> The interest in this field stems from both the inherent beauty of such systems as well as multiple potential applications in areas as diverse as host-guest chemistry, non-linear optics, magnetism, catalysis and the construction of molecular machines.<sup>6</sup> The introduction of “crossing points” to produce such topological complexity also has the potential to produce new materials’ properties; even some strands of DNA and various proteins have been found to be knotted.<sup>7</sup>

The controlled synthesis of these molecules can be

particularly challenging with many systems formed requiring careful design, templation or a degree of serendipity.<sup>1, 4</sup> While it is possible to design new periodic nets with the help of reticular methods<sup>5, 8</sup> and, to some extent, predict their properties using computational methods,<sup>9</sup> the applicability of these methods are often limited to systems in which symmetric ligands are to be employed. In part this stems from the many factors that influence self-assembly processes such as the variety in metal coordination numbers and ligand geometries, weak interactions between organic components and the synthetic conditions used.<sup>3, 10</sup> Polycarboxylate ligands are among the most widely used organic synthons for the preparation of MOFs,<sup>4, 11, 12</sup> since they provide strong and diverse coordination modes towards metal centres, leading to particularly robust frameworks which often display interesting magnetic properties.<sup>11, 13</sup>

With the aim of producing materials displaying either unusual topologies or physical properties, the rigid but non-symmetrical 2-sulfoterephthalate (**stp**) ligand has been used in combination with nitrogen co-ligands and transition metals or lanthanides to produce a number of discrete and polymeric materials.<sup>14</sup> The **stp** ligand presents a diverse number of potential coordination and bridging modes, along with multiple accessible protonation states due to the presence of both the carboxylate and the sulfonate groups.

As an extension of these studies, with the overarching aim of better understanding self-assembly in the formation of metal-organic frameworks in the present investigation, we

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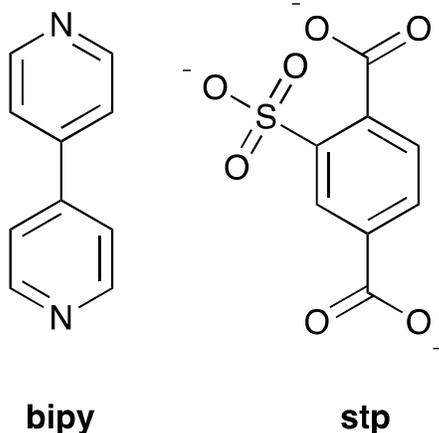
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† Electronic Supplementary Information (ESI) available: X-ray crystallographic files in CIF format, ORTEP drawings and molecular structure figures along with additional tables with selected geometrical parameters. See DOI: 10.1039/b000000x/

have employed **stp** and the rigid, nitrogen-containing 4,4'-bipyridine (**bipy**) in combination with cobalt(II) to form five structurally and topologically diverse materials. The connectivities of these materials depend on the ratios of starting materials employed. Their synthesis, characterisation and magnetic properties are reported.



## Experimental

### Materials

2-sulfoterephthalic acid monosodium salt Na(H<sub>2</sub>stp) (Acros Organics), 4,4'-bipyridine and cobalt nitrate hexahydrate (Aldrich) were used as received without further purification. Percentage yields are relative to the quantity of cobalt(II) employed.

### Physical techniques

Elemental analyses were performed on a Thermo Flash 2000 CHN-O elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 883-Infrared spectrophotometer in the range 4000–200 cm<sup>-1</sup> as KBr pellets. Magnetic susceptibility measurements were carried out with a Quantum Design SQUID MPMS-XL susceptometer apparatus working in the temperature range 2–300 K, under a magnetic field of 0.5 T. Pascal's constants were used to estimate diamagnetic corrections to the molar paramagnetic susceptibility.

### Synthesis

**Synthesis of {[Co<sub>3</sub>(stp)<sub>2</sub>(bipy)(H<sub>2</sub>O)<sub>4</sub>]}·2H<sub>2</sub>O (1).** A mixture of 2-sulfoterephthalic acid monosodium salt (0.0536 g, 0.20 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.7466 g, 6.0 mmol), 4,4'-bipyridine (0.0626 g, 0.40 mmol) and water (8 mL) was placed in a 25 mL stainless reactor with Teflon liner and heated to 160 °C for 48 h. Then, it was cooled down to room temperature at a rate of –6 °C/h. Pink crystals were separated by filtration, washed with deionised water and dried in air. Yield: 0.044 g (0.26 %). Anal. Calc. for C<sub>26</sub>H<sub>26</sub>Co<sub>3</sub>N<sub>2</sub>O<sub>20</sub>S<sub>2</sub>: C, 33.67; H, 2.83; N, 3.02. Found: C, 33.38; H, 3.04; N, 3.26. IR (KBr, cm<sup>-1</sup>): 3349, 2491, 1609, 1487, 1239, 1188, 1157, 1071, 1020, 860, 778, 625, 535, 525, 449, 437.

**Synthesis of {[Co<sub>3</sub>(stp)<sub>2</sub>(bipy)<sub>5</sub>(H<sub>2</sub>O)<sub>6</sub>]}·4H<sub>2</sub>O (2).** A mixture of 2-sulfoterephthalic acid monosodium salt (0.0402 g, 0.15 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0873 g, 0.30 mmol), 4,4'-bipyridine (0.2191 g, 1.40 mmol) and water (1.5 mL) was placed in a 25 mL stainless reactor with Teflon liner and heated to 160 °C for 48 h. Then, it was cooled down to room temperature at a rate of –6 °C/h. Orange coloured crystals were separated by filtration, washed with deionised water and dried in air. Yield: 0.051 g (31 %). Anal. Calc. for C<sub>66</sub>H<sub>66</sub>Co<sub>3</sub>N<sub>10</sub>O<sub>24</sub>S<sub>2</sub>: C, 48.81; H, 4.10; N, 8.62. Found: C, 48.27; H, 3.79; N, 8.41. IR (KBr, cm<sup>-1</sup>): 3407, 2932, 1970, 1603, 1561, 1385, 1242, 1176, 1069, 1009, 827, 663, 623, 538, 383.

**Synthesis of [Co<sub>3</sub>(stp)<sub>2</sub>(bipy)<sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>]}·8H<sub>2</sub>O (3).** A mixture of 2-sulfoterephthalic acid monosodium salt (0.0536 g, 0.20 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.5822 g, 2.0 mmol), 4,4'-bipyridine (0.1252 g, 0.80 mmol) and water (8 mL) was placed in a 25 mL stainless reactor with Teflon liner and heated to 120 °C for 48 h. Then, it was cooled down to room temperature at a rate of –6 °C/h. Yellowish-orange coloured crystals were separated by filtration, washed with deionised water and dried in air. Yield: 0.119 g (11 %). Anal. Calc. for C<sub>56</sub>H<sub>74</sub>Co<sub>3</sub>N<sub>8</sub>O<sub>32</sub>S<sub>2</sub>: C, 41.72; H, 4.63; N, 6.95. Found: C, 41.39; H, 4.47; N, 7.12. IR (KBr, cm<sup>-1</sup>): 3468, 2727, 1608, 1415, 1229, 1176, 1071, 1026, 920, 812, 682, 626, 530, 450, 393.

**Synthesis of [Co(Hstp)<sub>2</sub>(Hbipy)<sub>2</sub>]** (4). A mixture of 2-sulfoterephthalic acid monosodium salt (0.0536 g, 0.20 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2911 g, 1.0 mmol), 4,4'-bipyridine (0.2191 g, 1.40 mmol) and water (4 mL) was placed in a 25 mL stainless reactor with Teflon liner and heated to 140 °C for 48 h. Then, it was cooled down to room temperature at a rate of –6 °C/h. Yellow crystals were separated by filtration, washed with deionised water and dried in air. Yield: 0.089 g (10 %). Anal. Calc. for C<sub>36</sub>H<sub>26</sub>CoN<sub>4</sub>O<sub>14</sub>S<sub>2</sub>: C, 50.18; H, 3.04; N, 6.50. Found: C, 50.13; H, 3.27; N, 6.79. IR (KBr, cm<sup>-1</sup>): 3453, 2741, 1621, 1433, 1227, 1189, 1043, 1019, 933, 841, 705, 659, 511, 477, 403.

**Synthesis of {[Co(stp)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][Co(bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]}·2Hbipy·2H<sub>2</sub>O (5).** A mixture of 2-sulfoterephthalic acid monosodium salt (0.0536 g, 0.20 mmol), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2911 g, 1.0 mmol), 4,4'-bipyridine (0.0626 g, 0.40 mmol) and water (4 mL) was placed in a 25 mL stainless reactor with Teflon liner and heated to 160 °C for 48 h. Then, it was cooled down to room temperature at a rate of –6 °C/h. Yellow crystals were separated by filtration, washed with deionised water and dried in air. Yield: 0.102 g (15 %). Anal. Calc. for C<sub>56</sub>H<sub>56</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>22</sub>S<sub>2</sub>: C, 48.92; H, 4.10; N, 8.15. Found: C, 49.47; H, 4.53; N, 8.29. IR (KBr, cm<sup>-1</sup>): 3467, 2728, 1598, 1447, 1193, 1177, 1028, 937, 827, 722, 671, 526, 482, 397.

### Crystallography

Crystal data and experimental details for data collection and structure refinement are reported in Table 1. Intensity data and cell parameters were recorded at 293(2) K for **1** and **2**, and at 190(2) K for **3** and **4** on a Bruker APEX II (MoK $\alpha$  radiation  $\lambda$  = 0.71073 Å) equipped with a CCD area detector and a graphite monochromator.<sup>15</sup> The data of **5** were collected at 150(2) K with an Oxford Gemini Ultra.<sup>16</sup> Multi-scan absorption corrections were applied with either SADABS<sup>17</sup> or CrysalisPro<sup>16</sup>

and subsequent computations were carried out using the WinGX-32 graphical user interface.<sup>18</sup> The structures were solved by direct methods using either SHELXS-97<sup>19</sup> or SIR97<sup>20</sup> before refinement with SHELXL-97.<sup>19</sup> In general, full occupancy non-hydrogen atoms were refined with anisotropic atomic displacements and carbon-bound hydrogen atoms were included in idealised positions and refined using a riding atom. When possible, the water H-atoms were found in the difference Fourier map. Compound **3** contains a large region of diffuse solvent which could not be sensibly modelled and so

the SQUEEZE<sup>21</sup> function of PLATON<sup>22</sup> was employed. This residual electron density was assigned to eight molecules of water per unit cell.

Crystallographic data for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-894354 (**1**), -840729 (**2**), -894355 (**3**), -894356 (**4**) and -901677 (**5**) can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).



## Results and Discussion

### Synthesis and Structural Descriptions

Five coordination materials were prepared and structurally characterised.  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$  (1),

$\{[\text{Co}_3(\text{stp})_2(\text{bipy})_5(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}\}_n$  (2),

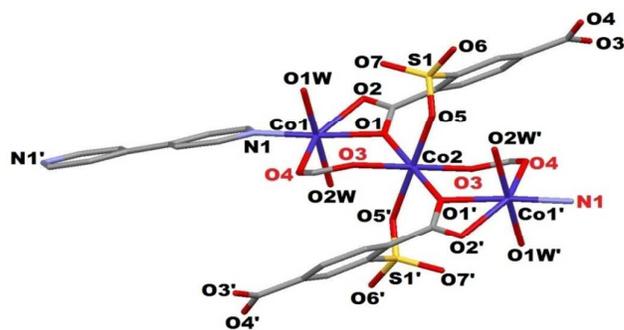
$[\text{Co}_3(\text{stp})_2(\text{bipy})_4(\text{H}_2\text{O})_{10}]\cdot 8\text{H}_2\text{O}$ , (3),  $[\text{Co}(\text{Hstp})_2(\text{Hbipy})_2]$ , (4) and

$\{[\text{Co}(\text{stp})_2(\text{H}_2\text{O})_2][\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]\cdot 2\text{Hbipy}\cdot 2\text{H}_2\text{O}$ , (5), were all

generated hydrothermally by a reaction between different molar ratios of cobalt(II) nitrate hexahydrate and a mixture of 2-sulfoterephthalic acid monosodium salt,  $\text{Na}(\text{H}_2\text{stp})$  and 4,4'-bipyridine (bipy) in water. Complexes 1 and 2 are coordination polymers, while 3, 4 and 5 are discrete coordination compounds. All the complexes are involved in extended networks of hydrogen-bonding interactions. From the distinct solid-state frameworks achieved, it is obvious that the stoichiometric ratio used in the synthesis has a significant influence on the molecular structure of the corresponding metal compound. Moreover, these five crystal structures highlight the various potential binding modes of the  $\text{NaH}_2\text{stp}$  ligand, which are enhanced by its different possible protonation states.

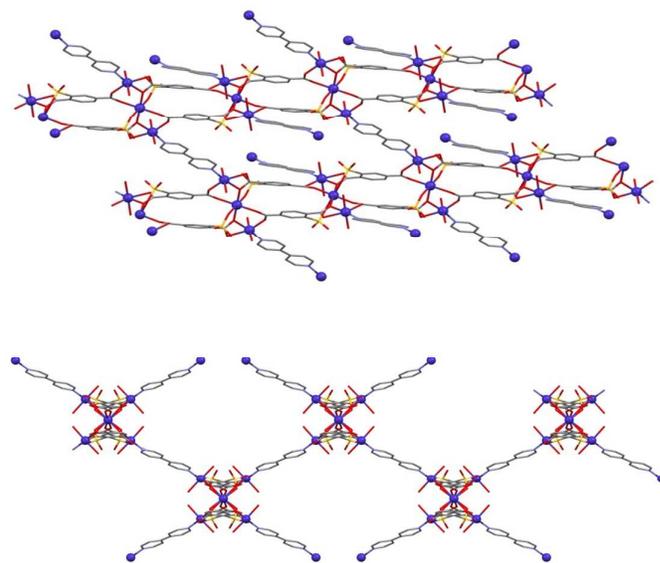
Compound 1 (Figures 1-3 and S1†), prepared using an excess of metal salt as reflected by the cobalt nitrate: $\text{NaH}_2\text{stp}$ :bipy ratio of 30:1:2, is a triply interpenetrated, three-dimensional coordination polymer with formula  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$ .

The infinite network is built up from  $[\text{Co}_3(\text{stp})_2(\text{bipy})(\text{H}_2\text{O})_4]$  units that are bridged to each other through two bipy and four stp ligands. Within each trinuclear unit, the three six-coordinated metal centres are bridged through four stp ligands resulting in an  $\text{O}_6$  coordination geometry for the central Co2 ion. The additional Co(II) ions (Co1 and the symmetry-related atom Co1') presents a highly distorted octahedral geometry, whose equatorial plane is occupied by one nitrogen atom from a bridging bipy ligand and three carboxylate oxygen atoms from two different stp ligands. Two water molecules are coordinated at the axial positions of the octahedron. One of the stp ligands binds to Co1 with both carboxylate oxygen atoms (O1 and O2), forming a four membered chelate ring, while the second stp ligand coordinates to Co1 through only one (O4) of its carboxylate oxygen atoms. The other oxygen atom from this carboxylate (O3) binds to the central metal centre of the tricobalt unit, *i.e.* Co2, which is also coordinated by O1 in a bridging  $\mu$ -fashion. The octahedral coordination geometry of Co2 is completed by two sulfonato groups (O5 and O5') at the axial positions (see Table 2 for selected bond distances and angles).



**Figure 1.** Symmetry-generated trinuclear unit building up the molecular structure of  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$  (1). The red-labeled atoms belong to adjacent units and are included to show the coordination environment around the metal centres. Hydrogen atoms and lattice water molecules have been omitted for clarity.

As mentioned above, the trinuclear units are bridged by both bipy and stp ligands to generate an infinite three-dimensional polymer. Hence, the stp ligands connect adjacent tricobalt units, forming parallel ribbon-like chains that propagate along the crystallographic *c*-axis (Figure 2 top). The close arrangement of the stp ligands is stabilised by strong offset face-to-face  $\pi$ - $\pi$  stacking interactions between neighbouring phenyl rings (centroid-to-centroid distance of 3.80 Å).



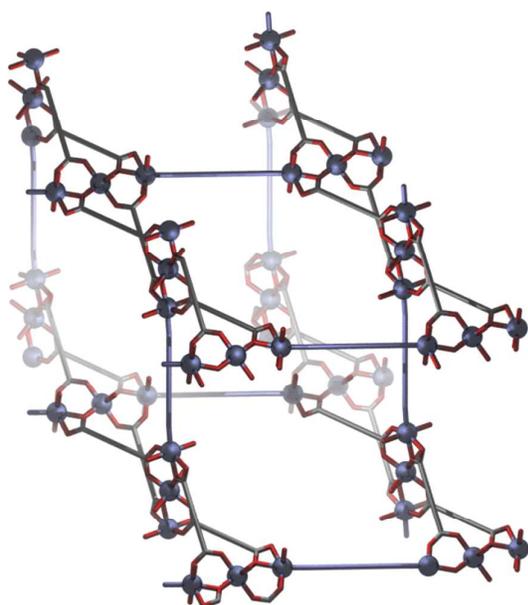
**Figure 2.** Top: view of the three-dimensional network in 1 along the crystallographic *b*-axis highlighting the one-dimensional ribbon-like chains formed by the stp ligands and the trinuclear units. Bottom: perspective view down the crystallographic *c*-axis (*i.e.* down the one-dimensional ribbon-like chains), illustrating the manner in which the bipy ligands connect the one-dimensional chains to form a three-dimensional network.

Neighbouring ribbon-like chains are in turn linked together through bipy ligands (see Figure 2 bottom). Thus, each chain is connected to four adjacent ones, producing a three-dimensional network that apparently exhibits large voids

(Figure 3). However, the network is not porous as it is in fact triply interpenetrated (Figure 4); this intricate arrangement is stabilised by  $\pi$ - $\pi$  stacking interactions between adjacent 3D coordination polymers and by a network of hydrogen bonds involving water molecules and oxygen atoms belonging to **stp** ligands (see Table S1 and Figure S2).

**Table 2.** Selected bond distances (Å) and angles (°) for  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$  (**1**)

Co1–O1W	2.079(6)	Co1–N1	2.072(9)	O1–Co1–O4	97.35(9)
Co1–O2W	2.227(9)	Co1–O4	2.055(9)	Co2–O1	2.041(6)
Co1–O1	2.100(9)	N1–Co1–O2	111.74(9)	Co2–O3	2.090(9)
Co1–O2	2.301(9)	O2–Co1–O1	58.46(9)	Co2–O5	2.144(6)



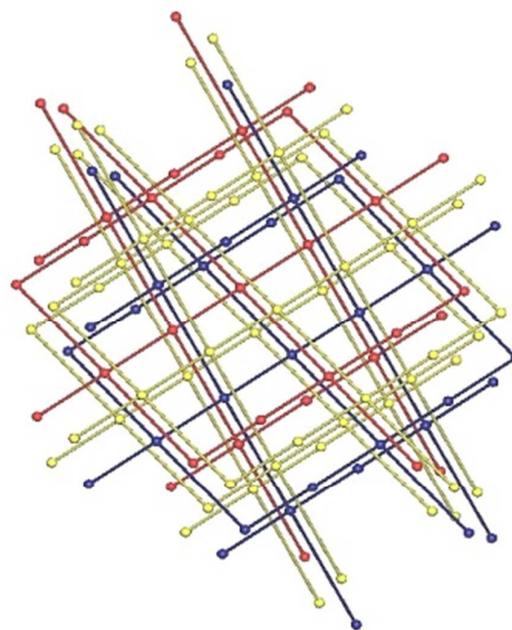
**Figure 3.** Schematic representation of the three-dimensional network in  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$  (**1**). The cobalt centres are shown as balls, the bipy ligands as blue sticks and the **stp** ligands as grey and red sticks.

If each of the trinuclear  $[\text{Co}_3(\text{stp})_2]$  units are considered clusters<sup>23</sup> connected by simple two-fold linear (bipy) connectors, then the topology<sup>24</sup> of **1** can be described as a 3-fold interpenetrated (Class Ia)<sup>25</sup> 4-connected net of the well-known type **cds** with point symbol  $\{6^5.8\}$  (see Figure 4).<sup>26</sup>

The same reaction, performed with a cobalt nitrate:stp:bipy ratio of 2:1:9.3 yielded the compound  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})_5(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**). The asymmetric unit of **2** is depicted in Figure S3. In contrast to **1**, the **stp** ligands in **2** do not bridge the metal centres, which are instead connected through the bipy units. Each cobalt(II) ion is octahedrally

coordinated (Figure 5). Co1 presents a  $\text{N}_3\text{O}_3$  coordination sphere, with the metal ion bound to two bridging bipy ligands, one non-bridging bipy, a water molecule and two oxygen atoms (one carboxylate and one sulfonate) from a chelating **stp** ligand (Figure 5).

Similarly, the geometry around Co2, which lies on an inversion centre, can be conveniently described as an octahedron with bipy ligands at the apical positions and four water molecules occupying the equatorial plane (see Table 3 for selected bond distances and angles). The bipy ligands coordinated to Co2 are bridging this central metal centre to two external cobalt atoms, *ie* Co1 and its symmetry-related counterpart Co1', generating a linear trinuclear  $[\text{Co}_3(\text{stp})_2(\text{bipy})_4(\text{H}_2\text{O})_6]$  unit (Figure 5).

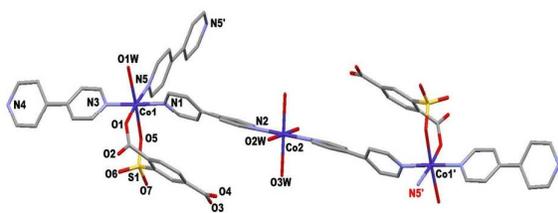


**Figure 4.** A simplified representation of the 3-fold interpenetrating **cds** net present in **1** (the three interpenetrating nets are highlighted in red, blue and yellow).

Adjacent trinuclear units are bridged by bipy ligands producing infinite one-dimensional zig-zag chains (see Figure 6). The crystal packing of **2** features intra-monomer (a monomer being a trinuclear unit; see Figure 5) and inter-monomer  $\pi$ - $\pi$  interactions, and hydrogen-bonding contacts between water molecules and **stp** oxygen atoms and between a water molecule and the uncoordinated nitrogen atom from bipy (see Figure S4 and Table S2).

Applying a cobalt nitrate:stp:bipy ratio of 10:1:4, the discrete trinuclear complex  $[\text{Co}_3(\text{stp})_2(\text{bipy})_4(\text{H}_2\text{O})_{10}] \cdot 8\text{H}_2\text{O}$ , (**3**) is obtained (whose asymmetric unit is shown in Figure S5). The trinuclear moiety of this compound is comparable to that of **2**. In the case of **3**, however, one of the bridging bipy ligands is replaced by a coordinated water molecule, thus yielding a discrete complex instead of a coordination polymer. Each metal center presents an octahedral geometry with a  $\text{N}_2\text{O}_6$

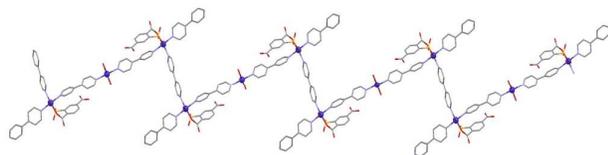
coordination sphere. Co1 is bound to both a bridging and a non-bridging bipy ligand, a monodentate **stp** ligand and three aqua ligands (Figure 7).



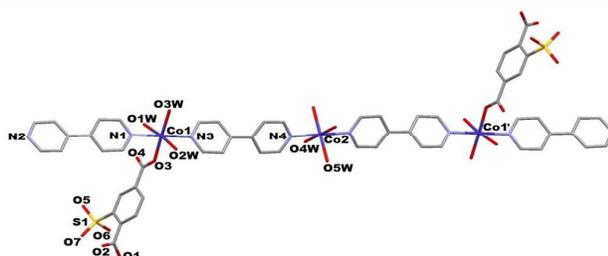
**Figure 5.** Symmetry-generated unit of the coordination polymer  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})_5(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**). The nitrogen atom labelled in red belongs to an adjacent unit and is included to show the coordination environment around Co1'. Hydrogen atoms and lattice water molecules have been omitted for clarity.

**Table 3.** Selected bond distances (Å) and angles (°) for  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})_5(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**)

Co1–N1 2.164(2)	Co1–O5 2.082(2)	Co2–O3W 2.118(2)
Co1–N3 2.168(2)	Co1–O1W 2.099(2)	O5–Co1–O1W 173.46(8)
Co1–N5 2.151(2)	Co2–N2 2.213(2)	N1–Co1–N3 176.35(9)
Co1–O1 2.138(2)	Co1–O2W 2.049(2)	N5–Co1–O1 173.79(8)



**Figure 6.** View of the one-dimensional polymer observed in the solid-state structure of  $\{[\text{Co}_3(\text{stp})_2(\text{bipy})_5(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**). Metal centres are represented as blue spheres. Hydrogen atoms and lattice water molecules have been omitted for clarity.



**Figure 7.** The symmetry-generated trinuclear complex  $[\text{Co}_3(\text{stp})_2(\text{bipy})_4(\text{H}_2\text{O})_{10}] \cdot 8\text{H}_2\text{O}$  (**3**). Hydrogen atoms and lattice water molecules have been omitted for clarity.

As in **2**, Co2 is bound to two bridging bipy ligands and four equatorial water molecules (see Table 4 for selected bond distances and angles). The water molecules coordinated to the metal centres are involved in an intricate network of hydrogen bonds which stabilise the complexes in the lattice (see Figures

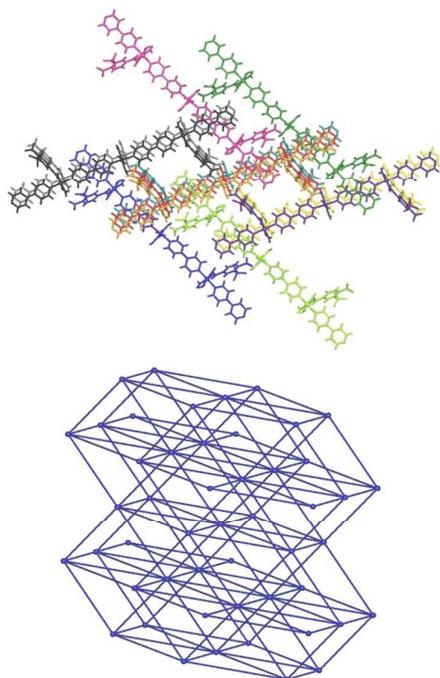
S6 and S7 in the Supporting Information). Indeed, the topological analysis of the intermolecular H-bonding interactions shows that the complexes form a supramolecular 10-connected, uninodal **bct** type net, with point symbol  $\{3^{12}.4^{28}.5^5\}$  (see Figure 8).

The mononuclear compound  $[\text{Co}(\text{Hstp})_2(\text{Hbipy})_2]$  (**4**) was obtained by increasing the amount of bipy in the reaction, namely using a cobalt nitrate:stp:bipy ratio of 5:1:7. As for the previous complexes, the cobalt(II) centres in **4** exhibit octahedral coordination environments (see Figures 9 and S8). The metal ions are coordinated by two doubly deprotonated 2-sulfoterephthalic groups acting as bidentate ligands through sulfonate and carboxylate oxygen donors (see Table 4 for selected bond distances and angles), thus forming seven-membered chelate rings similar to that observed in **2**.

The axial positions are occupied by two monoprotonated bipy ligands (See Figure 9) that form intramolecular  $\pi$ - $\pi$  stacks with the **stp** ligands. Adjacent complexes are connected through hydrogen-bonding contacts between the Hbipy hydrogen atom and two oxygen atoms, from a carboxylic and a sulfonate groups. In addition, the mononuclear units are involved in  $\pi$ - $\pi$  interactions; all these supramolecular interactions generate two-dimensional layers that propagate perpendicularly to the crystallographic *ac*-plane (Figure 10 top).

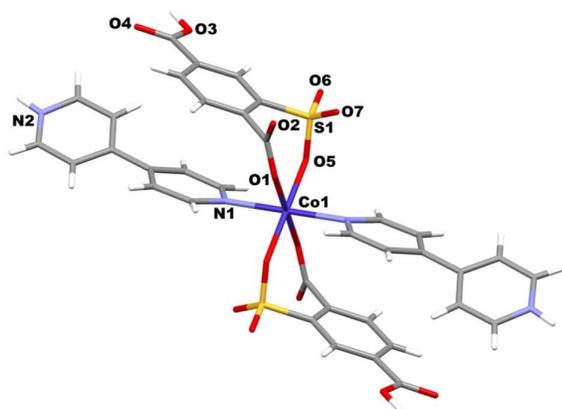
**Table 4.** Selected bond distances (Å) and angles (°) for  $[\text{Co}_3(\text{stp})_2(\text{bipy})_4(\text{H}_2\text{O})_{10}] \cdot 8\text{H}_2\text{O}$  (**3**) and  $[\text{Co}(\text{Hstp})_2(\text{Hbipy})_2]$  (**4**).

3		
Co1–N1 2.135(2)	Co1–O2W 2.117(2)	Co2–O5W 2.074(2)
Co1–N3 2.143(2)	Co1–O3W 2.054(2)	N1–Co1–N3 178.87(6)
Co1–O3 2.052(1)	Co2–N4 2.147(2)	O3–Co1–O3W 178.07(6)
Co1–O1W 2.136(2)	Co2–O4W 2.115(2)	O1W–Co1–O2W 174.14(6)
4		
Co1–N1 2.158(2)	Co1–O5 2.102(1)	O1–Co1–O5 95.01(6)
Co1–O1 2.061(1)	N1–Co1–O1 93.74(5)	N1–Co1–O5 87.86(6)

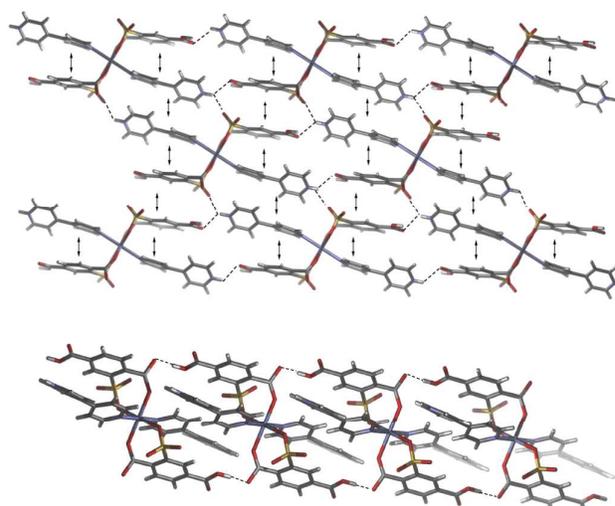


**Figure 8.** Top: ten neighbouring molecules surround the trinuclear complex **3** taken as reference (in red) through a network of hydrogen bonds. Bottom: schematic representation of the 10-c, uninodal **bct** net.

These layers are linked by strong hydrogen bonds, taking place between two of the carboxylic acid groups of the **Hstp** ligands [O3...O2 2.497(2) Å] and the protonated bipy ligands, producing infinite ribbon-like chains along the crystallographic *b*-axis (Figure 10 bottom), and thus an infinite three-dimensional lattice.



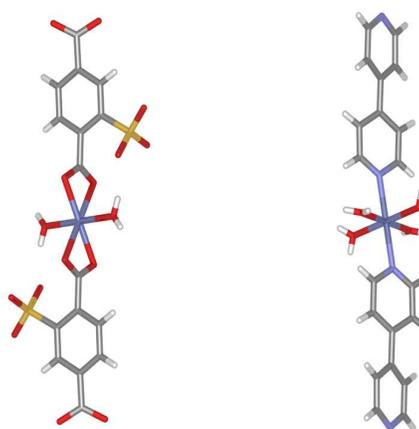
**Figure 9.** The molecular structure of [Co(Hstp)<sub>2</sub>(Hbipy)<sub>2</sub>] (**4**).



**Figure 10.** Top: two-dimensional layer in **4** generated by means of hydrogen bonds (represented as dashed lines) and  $\pi$ - $\pi$  interactions (arrows). Bottom: one-dimensional ribbon-like chains formed through strong hydrogen bonds between the carboxylic groups of the **Hstp** ligands (dotted lines).

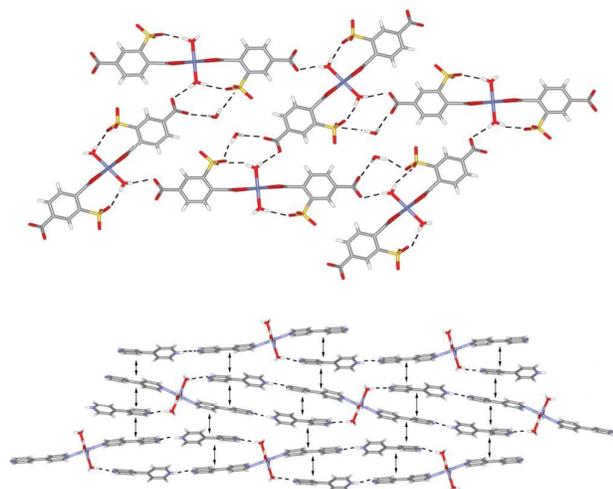
The use of a cobalt nitrate:**stp**:bipy ratio of 5:1:2 resulted in the formation of the ionic compound {[Co(**stp**)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][Co(bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]}·2Hbipy·2H<sub>2</sub>O (**5**). The cobalt(II) center in the [Co(**stp**)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>4-</sup> anion presents an O<sub>6</sub> coordination sphere with two coordinated water molecules and two **stp** ligands coordinating in a bidentate fashion through their 1-carboxylate groups, giving rise to 4-membered chelate rings (Figure 11). The charge of this anionic complex is balanced by a [Co(bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> cation and two protonated Hbipy cations.

In a similar fashion to the corresponding units observed in **2** and **3**, the metal centre in [Co(bipy)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> is octahedral with aqua ligands in the equatorial plane (Figure 11). The two axial bipy ligands are monodentate (and therefore non-bridging).

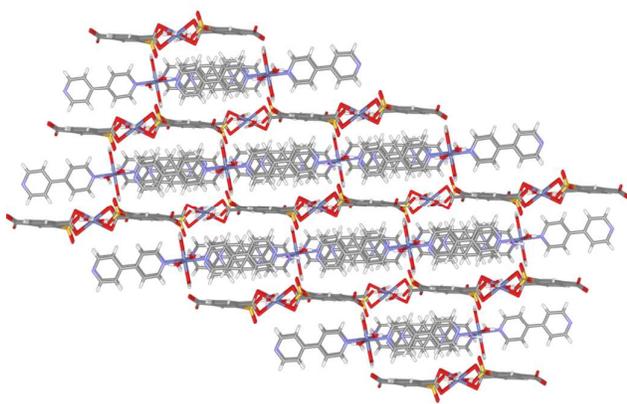


**Figure 11.** Anionic  $[\text{Co}(\text{stp})_2(\text{H}_2\text{O})_2]^{4-}$  (left) and cationic  $[\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$  (right) complexes found in compound **5**.

The anionic  $[\text{Co}(\text{stp})_2(\text{H}_2\text{O})_2]^{4-}$  complexes and the water molecules interact through hydrogen bonds, producing infinite two-dimensional layers (Figure 12 top). The cationic  $[\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$  complexes and the Hbipy molecules are also assembled supramolecularly through a combination of strong hydrogen bonding and  $\pi$ - $\pi$  interactions, yielding comparable layers (Figure 12 bottom). The solid-state structure of **5** is thus formed by both positively and negatively charged layers. Each of the charged layers is arranged alternately in the crystal lattice, with additional hydrogen bonds connecting them to form an infinite three-dimensional framework (Figure 13).



**Figure 12.** Top: two-dimensional network of  $[\text{Co}(\text{stp})_2(\text{H}_2\text{O})_2]^{4-}$  anions in **5**. Bottom: two-dimensional network of  $[\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$  together with Hbipy<sup>+</sup> cations in **5**. The dashed lines represent the hydrogen bonds, and the arrows the  $\pi$ - $\pi$  interactions.



**Figure 13.** The infinite three-dimensional network in **5** viewed along the layers depicted in Figure 12.

### Structural Juxtaposition

Five new complexes were synthesised hydrothermally using the same reactants but with distinct ratios. These compounds exhibit diverse structures, which include a triply interpenetrated three-dimensional coordination network (**1**), a one-dimensional coordination polymer (**2**), discrete coordination complexes (**3–4**), and an ionic complex (**5**). The diversity of the solid-state structures achieved reflects the high versatility of coordination modes and protonation states of both the **stp** and **bipy** ligands, the important involvement of coordinated water molecules through stabilising hydrogen-bonding interactions, and the crucial role played by the different amounts (*e.g.* concentrations and ratios) of reactants used for the preparation of the compounds.

In the solid-state structure of **1**, for which a large excess of metal salt was employed (Co/**stp** = 30/1 and Co/**bipy** = 15/1; see Table 5), each **stp** ligand is involved in six coordination bonds and acts as bridges between metal centres. It can be noted that for all other compounds, the **stp** ligands are not bridging and are involved in no more than two coordination bonds. The **stp**/**bipy** ratio used in the synthesis of **1**, *i.e.* 2/1, is found as well in its molecular structure.

When the amount of cobalt salt is significantly decreased (from 6 mmol to 1 mmol; see Table 5, respectively compounds **1** and **5**), keeping the quantities of **stp** and **bipy** identical to those used for **1** (see Table 5), the ionic compound **5** is produced. Amazingly, while the ratios Co/**stp** and Co/**bipy** are respectively 1/0.67 and 1/0.33 for **1**, these are 1/1 and 1/2 for **5** (see molecular formulae of **1** and **5**, respectively). Thus, the decrease in metal amount appears to favor the incorporation of more **bipy** into the final product **5** that is not a coordination polymer, in contrast to **1**.

If the **bipy**/Co ratio is increased further in the reaction mixture, from 0.4/1 (compound **5**) to 1.4/1 (compound **4**), the ionic complex **5** is converted to the mononuclear complex **4**, which contains two **bipy** ligands per metal centre as **5**. Thus, the excess of **bipy** (compared to the other two reactants, *i.e.* cobalt(II) nitrate and  $\text{NaH}_2\text{stp}$ ) used during the synthesis has a drastic effect on the molecular structure of the final compound. Actually, this excess appears to avoid the coordination of water molecules and even the presence of water molecules in the lattice.

A significant increase of the **bipy**/Co ratio, from 1.4/1 to 4.67/1 (see compounds **4** and **2**, respectively; Table 5) produces a radically distinct framework, namely a 1D infinite chain (compound **2**), which moreover includes coordinated and lattice water molecules (contrary to **4**, which does not contain water molecules). It has to be mentioned here that, while the concentrations  $[\text{NaH}_2\text{stp}]$  and  $[\text{bipy}]$  used for the preparation of **2** and **4** are practically identical, that of  $[\text{Cobalt}]$  has been decreased by a factor of 3 (Table 5). Accordingly, the concentrations of the various reactants employed during the synthesis obviously have also an influence on the structure of the ensuing material.

Finally, when the amount of **bipy** used is decreased (from 1.4 to 0.8 mmol) while that of cobalt is increased (from 0.3 to 2 mmol), compound **3** is obtained (instead of **2**), whose formula

is related to that of **2** (Table 5). Comparatively, the structure of **3** includes one bipy ligand less and contains 8 additional water molecules. Moreover, while **2** is a 1D coordination polymer, **3** is a discrete trinuclear cluster molecule.

### Variable Temperature Magnetic Measurements

Variable temperature magnetisation measurements under a constant magnetic field of 0.5 T were carried out in the 2-300 K range for compounds **1**, **2**, **3** and **5**. The corresponding  $\chi_M T$  versus  $T$  curves are represented in Figure 14. According to the structural characterisation, each compound exhibits their Co(II) centres in an octahedral environment, which implies them to be in a  $^4T_{1g}$  ground state.

**Table 5.** Molar ratios of reagents employed in the hydrothermal syntheses of **1**–**5**.

Compound	Quantity of reagents used (mmol)		
	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	NaH <sub>2</sub> stp	bipy
<b>1</b>	6	0.2	0.4
<b>2</b>	0.3	0.15	1.4
<b>3</b>	2	0.2	0.8
<b>4</b>	1	0.2	1.4
<b>5</b>	1	0.2	0.4

Therefore, a non-negligible influence of the orbital angular momentum to their magnetic properties is expected. This was considered for most of the compounds as a second order perturbation leading to significant zero-field splitting (ZFS) of the ground state, and also was included into significant deviations of the  $g$  value from the spin-only value. The corresponding Hamiltonian, which thus considers the Zeeman Effect and the axial ( $D$ ) and rhombic ( $E$ ) ZFS parameters, is that from equation E1.

$$H = \sum_{i=1}^N B_{2i}^0 O_{2i}^0 + \sum_{i=1}^N B_{2i}^2 O_{2i}^2 + \mu_B \sum_{i=1}^N g_i S_i B \quad (\text{E1})$$

In this equation,  $N$  is the number of centres in the complex, and  $B_2^2$  and  $B_2^0$  values are considered the same for all the centres. The zero-field splitting parameters were calculated as  $D = 3B_2^0 O_2^0$  and  $E = B_2^2 O_2^2$ .

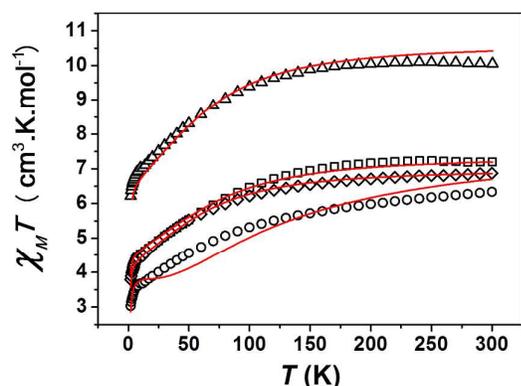
For the case of **1**, the metals exhibit significant magnetic coupling, and including it into this models renders it intractable, since reasonable fits could not be obtained. Thus, a very approximate model including the exchange interaction was used, where some of the spin-orbit coupling effects would be absorbed by the value of  $g$ . Thus, for this compound, the corresponding equation is E2 where  $S_1$ ,  $S_2$  and  $S_{1'}$  are the spin

operators for Co1, Co2 and Co1' and are assumed to have values of 3/2:

$$H = -2J(S_1 S_2 + S_2 S_{1'}) \quad (\text{E2})$$

The  $\chi_M T$  versus  $T$  curve of compound **1** exhibits a  $\chi_M T$  value at 300 K of 6.35 cm<sup>3</sup> K mol<sup>-1</sup>, which decreases upon lowering the temperature due to the effects of the spin-orbit coupling and antiferromagnetic interactions between the Co(II) ions. The drop observed at lower temperatures can be ascribed to the contribution of the ZFS, reaching a value of 3.03 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. The value of  $\chi_M T$  at high temperatures is greater than that expected for three Co(II) centres with  $S = 3/2$  and  $g = 2$  (calculated as 5.63 cm<sup>3</sup> K mol<sup>-1</sup>), demonstrating the contribution of the orbital angular momentum of the Co(II) ions. As mentioned above, any attempts of adding both spin-orbit and exchange-coupling parameters in the model led to unreasonable values. Thus, in order to estimate the interaction between the metal ions, the data were modelled without considering the contribution of ZFS and including, instead an additional  $J'$  parameter to model the decrease of  $\chi_M T$  product at low temperatures (which can be due in part to ZFS). This was performed by diagonalisation of the Hamiltonian in equation 2, using the program PHI.<sup>27</sup> Due to the very approximate nature of this model, a fit was not of good quality and can only serve as a way to estimate the magnitude of the exchange coupling. The parameters obtained were  $J = -11.95$  cm<sup>-1</sup> and  $g = 2.55$  with  $J'$  fixed at  $-0.02$  cm<sup>-1</sup>.

Complexes **2** and **3** show a value of  $\chi_M T$  of 10.04 and 7.20 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K, respectively, again higher than that expected for three independent Co(II) ions due to the influence of the orbital angular momentum. For both compounds, the  $\chi_M T$  value slightly diminishes down to 150 K, when a faster decline occurs down to 6.22 and 3.91 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K (for **2** and **3**, respectively). As the Co···Co separations are significant, the decline of the  $\chi_M T$  product upon cooling can be ascribed to spin-orbit coupling effects. At lower temperatures, the faster decline of the curve can be related to the contribution from the ZFS, associated to the axial elongation of the octahedral environment. Reasonably good fits were obtained with the following parameters:  $D = 74.1$  cm<sup>-1</sup>,  $E = -8.7$  cm<sup>-1</sup>,  $g = 2.74$  and  $D = 82.5$  cm<sup>-1</sup>,  $E = -4.2$  cm<sup>-1</sup>,  $g = 2.28$  for complexes **2** and **3**, respectively.



**Figure 14.**  $\chi_M T$  versus  $T$  curves of compounds **1** (○), **2** (Δ), **3** (□) and **5** (◇) at a constant field of 0.5 T. The solid lines are fits to the experimental data using an approximate model (see text).

For compound **5**, the value of  $\chi_M T$  at 300 K is  $6.87 \text{ cm}^3 \text{ K mol}^{-1}$ , significantly higher than that expected for two non-interacting  $S = 3/2$  centres ( $3.75 \text{ cm}^3 \text{ K mol}^{-1}$  for  $g = 2$ ). The curve gradually declines down to  $6.44 \text{ cm}^3 \text{ K mol}^{-1}$  at 130 K due to the effect of the spin-orbit coupling of the two Co(II) centres, since no possible interactions between the two ions can occur. At lower temperatures, a more abrupt drop of the  $\chi_M T$  product due to the ZFS is observed. In this case, the best fit parameters were  $D = 69.6 \text{ cm}^{-1}$ ,  $E = -10.0 \text{ cm}^{-1}$  and  $g = 2.73$  considering  $N = 2$ .

The high  $D$  values observed here are in agreement with complexes featuring metal ions with a quartet ground state and first order orbital moment, since the latter is in part incorporated into  $D$ .<sup>28</sup> In view of these results, dynamic susceptibility measurements were carried out to evaluate the possible slow magnetic relaxation of these systems. For all four compounds, no signal was found in the imaginary part of the ac susceptibility, thus showing that these systems do not show slow relaxation of the magnetisation.

## Conclusions

Five Co(II) coordination compounds derived from the combination of cobalt(II), **stp** and **bipy** in different ratios were prepared and characterised. The structures formed display diverse topologies ranging from discrete ionic complexes to three-dimensional coordination polymers depending on the ratios of reagents employed. The diversity of the solid-state structures derives from the versatility of coordination modes and protonation states of both the **stp** and **bipy** ligands combined with the participation of coordinated water molecules in both intra- and intermolecular hydrogen-bonding interactions. Temperature dependent magnetic measurements showed that compounds **1**, **2**, **3** and **5** have significant orbital angular momentum contributions.

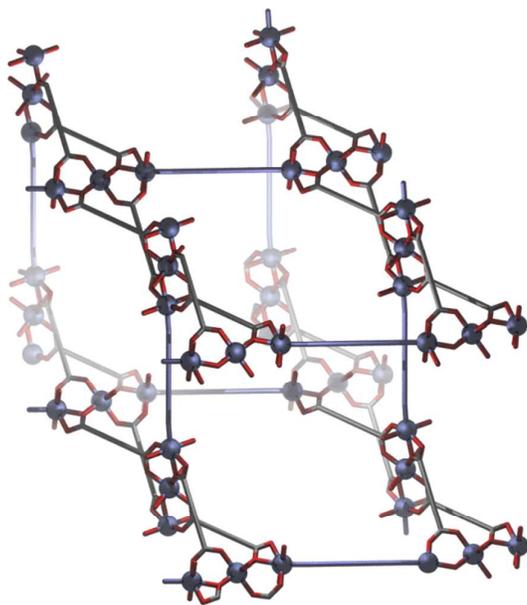
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Five discrete and polymeric complexes have been prepared and characterised from the reaction of different ratios of Co(II), 4,4'-bipyridine and 2-sulfoterephthalate.