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Old dog, new tricks: 2,2'-biphenol as a bridging and book-end ligand in discrete and extended Co(II) architectures**

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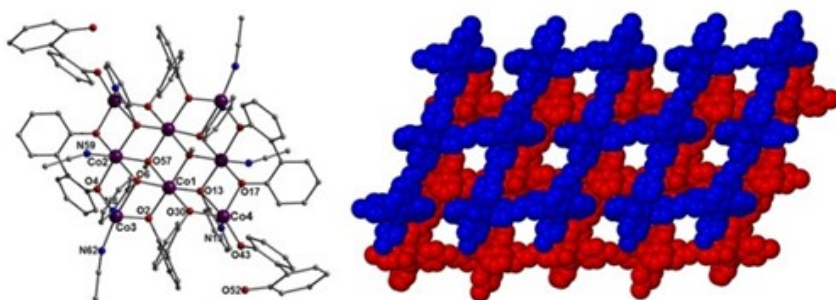
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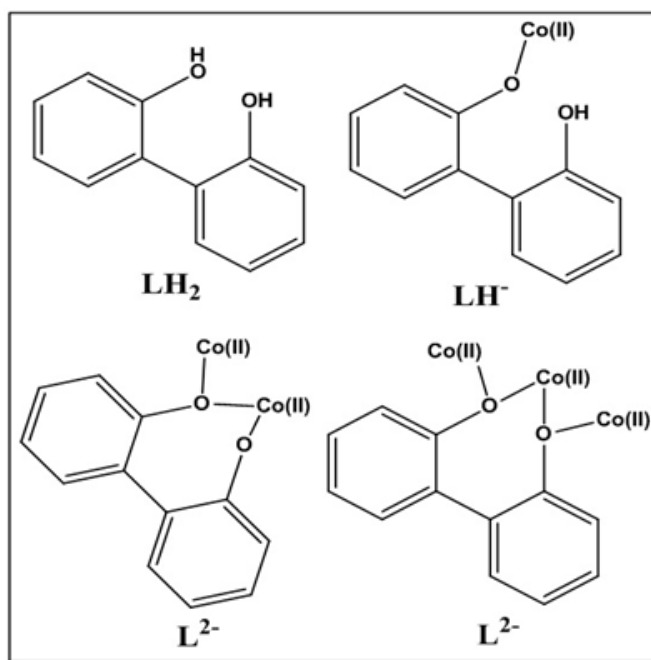


Abstract

We report the first Co(II) based discrete and extended network materials comprising the 2,2'-biphenol ligand. We first present the synthesis and magnetic characterisation of the Co(II) dinuclear complexes $[\text{Co(II)}_2(\text{L})_2(\text{py})_4] \cdot 2\text{EtOH}$ (**1**) and $[\text{Co(II)}_2(\text{L})_2(4\text{-pic})_4] \cdot 2\text{LH}_2$ (**2**), both of which exhibit antiferromagnetic exchange between their Co(II) centres. The introduction of the co-ligand 2-hydroxypyridine (2-hpH) leads to the production of planar octametalllic complex $[\text{Co(II)}_8(\text{OMe})_2(\text{L})_4(\text{LH})_2(2\text{-hp})_4(\text{MeCN})_4] \cdot \text{MeCN}$ (**3**). Magnetic susceptibility and magnetisation measurements on **3** indicate dominant ferromagnetic exchange between the Co(II) centres. We also describe the first Co(II) / 2,2'-biphenol extended networks in the shape of the 1D coordination polymer $\{[\text{Co(II)}(\text{LH})(4,4\text{-tmdp})_2(\text{NO}_3)](\text{LH}_2)\}_n$ (**4**) (where 4,4'-tmdp = 4,4'-trimethylenedipyridine) and the 2D brickwall network $[\text{Co(II)}(\text{LH})(\text{trans-bpe})_{1.5}(\text{NO}_3)]$ (**5**) (where trans-bpe = trans-1,2-bis(4-pyridyl)ethylene), comprising T-shaped nodes.

Introduction

The use of polyphenolic ligands in coordination chemistry is wide reaching and has enriched many areas of synthetic inorganic chemistry. For instance the vast field of molecular magnetism¹ and more pertinently its sub-topics Single-Molecule Magnetism,² molecular coolant materials³ and coordination polymers⁴ predominantly utilise O-rich aliphatic and aromatic ligands to construct their paramagnetic polymetallic assemblies.⁵ More specifically the O-donor atoms within these bridging OR (where R = aliphatic or aromatic group(s)) species are able to connect as many as three metal centres, lending themselves to the production of large polymetallic paramagnetic arrays. Moreover when polyphenolic ligands are used to form such magnetic clusters, their aromatic regions are able to act as organic sheaths, protecting the metal oxide rich core from potential hydrolysis as well as aiding crystallisation (during their inception), deterring intermolecular exchange (towards *magnetic dilution*) and increasing their organic solvent solubility towards further mechanical manipulation such as surface coating.⁶ Our own recent work in the field of molecular magnetism has focused on investigating the 1st row d-block coordination chemistry of the polyphenolic ligand 2,2'-biphenol (LH₂; Scheme 1). This has been extremely fruitful and encompasses (up to now) the production of a family of ionic and covalent $[\text{-Na(I)-M(III)-}]_n$ coordination polymers (M = Mn, Fe)⁷ and a series of bis- μ -alkoxide bridged Mn(III) dinuclear complexes used in an extensive MO and DFT study towards magneto-structural correlations.⁸



Scheme 1. Structure of the ligand 2,2'-biphenol (LH_2 : top left) and the bonding modes it exhibits in this work under various levels of deprotonation.

Results and Discussion

We present here a set of related complexes representing the first Co(II) species to be built using 2,2'-biphenol (LH_2). Interestingly this ligand is shown to exhibit all three accessible levels of deprotonation on producing these polymetallic architectures and will be shown to consistently bridge multiple Co(II) ions, as well as on occasion remaining neutrally charged and acting as a H-bonding book-end ligand. All crystal data described in this work is documented in Tables 1 (complexes **1-4**) and S1 (**5**). We first highlight the synthesis of the analogous dimeric complexes $[Co(II)_2(L)_2(py)_4] \cdot 2EtOH$ (**1**) and $[Co(II)_2(L)_2(4-pic)_4] \cdot 2(LH_2)$ (**2**) (where py = pyridine and $4-pic$ = 4-picoline). Both are produced by reaction of $Co(NO_3)_2 \cdot 6H_2O$ and 2,2'-biphenol in an EtOH / pyridyl ligand solvent mixture (pyridine in **1** and 4-picoline in **2**), along with a suitable base. Both **1** and **2** crystallise in the triclinic P-1 space group, with each possessing one $\{Co(II)_2\}$ unit in the asymmetric unit alongside one EtOH solvent of crystallisation and one neutral 2,2'-biphenol ligand (LH_2), respectively. The cores in **1** and **2** comprise two distorted trigonal bipyramidal Co(II) centres ($\tau = 0.67$ in both **1** and **2**) linked *via* two $\eta^1:\eta^2,\mu$ -bridging doubly deprotonated 2,2-biphenol ligands which produce Co \cdots Co distances of 3.164 and 3.167 Å, respectively (Fig. 1). The +2 cobalt oxidation state assessment was carried out *via* BVS calculations in conjunction with bond length and charge balancing

considerations. The coordination spheres at the metal centres are occupied by four terminally bound N-donor ligands ranging in Co(II)-N bond lengths of between 2.073 (Co1-N1 in **1**) and 2.157 Å (Co1-N2 in **1**). The Co(II)-O bond lengths in these siblings lie in the 1.949-2.072 Å range (Fig. 1).

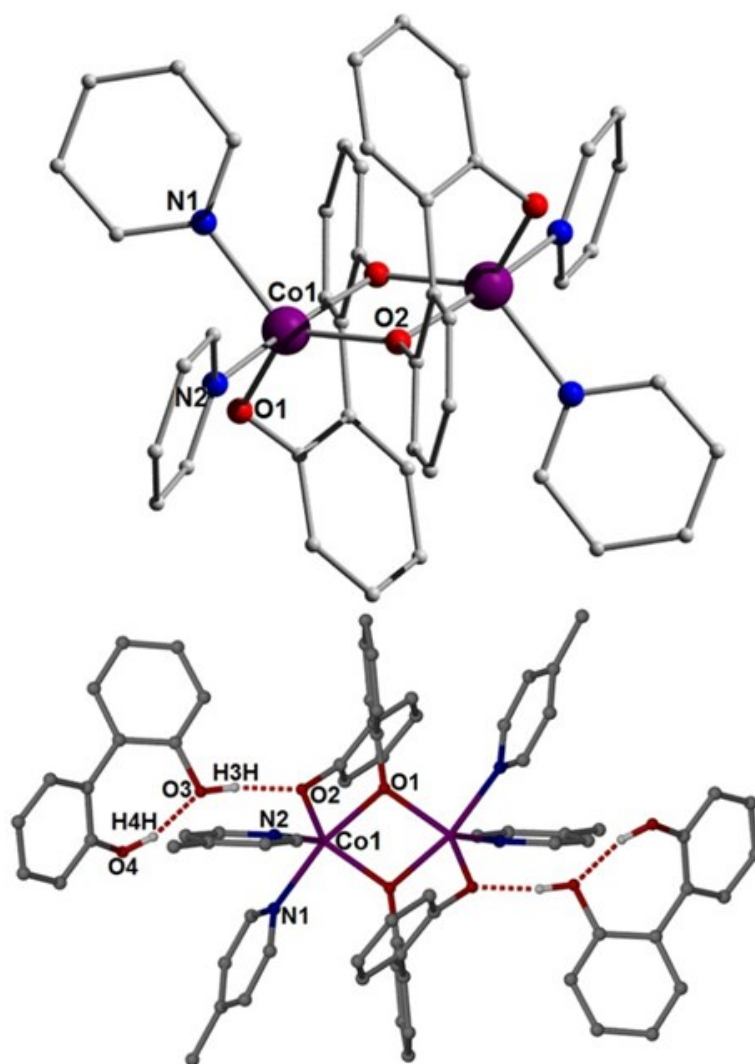


Figure 1. Crystal structures of **1** (top) and **2** (bottom) respectively. Colour code: Co (purple), O (red), N (blue), C (grey). Hydrogen atoms have been omitted for clarity. Colour code used throughout the text.

Interestingly the only difference between the two analogues lies in their peripheral connectivity. Two EtOH solvent molecules reside outside the first coordination sphere in **1**. In complex **2** however there are two neutral, crystallographically related, 2,2'-biphenol ligands which act as molecular book ends

held *via* intermolecular H-bonding interactions. More specifically the phenolic protons of each LH₂ (H3H and symmetry equivalent (s.e)) strongly interact with the phenolic O-atoms (O2 and s.e) of the bridging L²⁻ ligands (O3(H3H)⋯O2 = 1.694 Å) (Fig. 1). An intramolecular H-bond within the LH₂ ligands is also seen at a distance of O4(H4H)⋯O3 = 1.858 Å. These neutral book ends further interact with one another *via* symmetry equivalent H bonds through their phenolic O- and H-atoms (O4⋯H4H' = 2.504 Å). Moreover these nearby LH₂ units also act as book-end ligands for the neighbouring {Co(II)}₂ moieties in **2**, resulting in superimposable -{Co(II)}₂-LH₂-LH₂-{Co(II)}₂- rows (Fig. 2). These chains then assemble in the common space efficient brickwork arrangement within the unit cell and are also superimposable along the *a* axis. The packing in **1** comprises the superimposable stacking of the individual {Co(II)}₂ units along the *b* axis of the cell. These columns then also arrange in a brickwork fashion and are linked *via* off-set inter-chain π-π stacking interactions between juxtaposed pyridine ligands (C13-C17⋯C13'-C17' = 3.985 Å) (Fig. S1). The result of these spacer EtOH and LH₂ moieties in **1** and **2** are intra-chain Co⋯Co distances of 15.14 Å and 10.96 Å, respectively (Fig. 2), while their corresponding inter-chain distances lie at 8.38 Å in **1** and 9.36 Å in **2**.

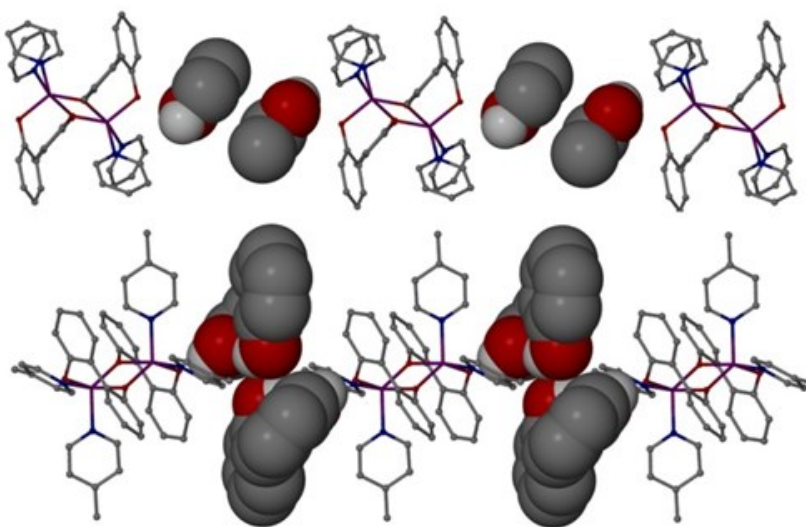


Figure 2. Views perpendicular to the superimposable rows within the cells of **1** (top) and **2** (bottom) showing the EtOH solvents (in **1**) and book-end 2,2'-biphenol ligands (LH₂ in **2**), both depicted in space-fill mode.

The $\eta^1:\eta^2,\mu$ -bonding mode of L²⁻ has been observed on numerous occasions in the linking of 1st row heterovalent TM ions,⁹ however the production of **1** and **2** highlights the rarer occurrence of the bridging of two homovalent 1st row ions.^{10,11} Moreover the ability of the 2,2'-biphenolate ligands to exhibit the $\eta^1:\eta^2,\mu$ -bridging motif in **1** and **2**, as opposed to the regularly adopted chelating

mode as seen in our recently reported family of μ -OR bridged [Mn(III)₂] dimers,⁸ persuaded us to pursue the production of polynuclear Co(II) complexes using LH₂. A perusal of the literature regarding the production of such multimetallic cluster compounds will show that the majority of such assemblies are complimented with more than one organic ligand. Thus a sensible approach for us was the introduction of a secondary ligand with metal bridging capabilities in the form of 2-hydroxypyridine (2-hpH). Much to our delight the immediate result was the production of the octametallc complex [Co(II)₈(OMe)₂(L)₄(LH)₂(2-hp)₄(MeCN)₄·MeCN (**3**) (Fig. 3), whose existence represents the second largest cluster ever reported using 2,2'-biphenol, behind the decametallc [NMe₄]₄[Mn₁₀O₄(L)₄X₁₂] (where X = Cl, Br) clusters reported by Lippard and co-workers.^{9b,9c}

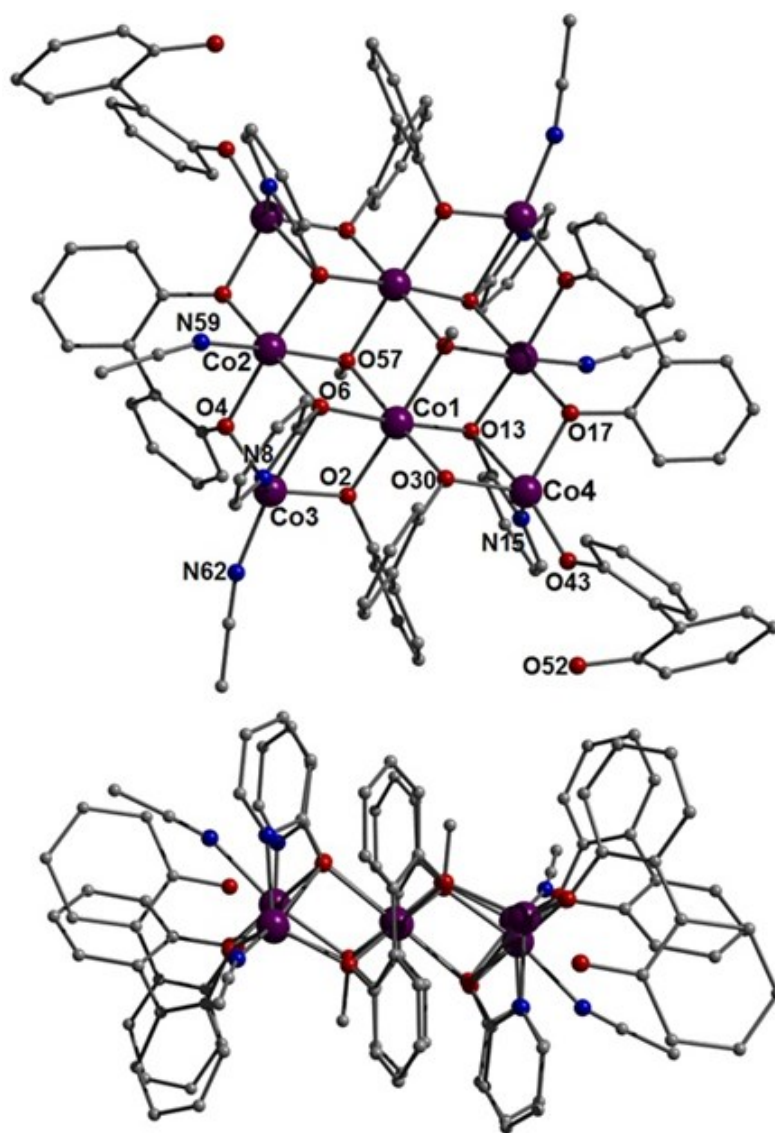


Figure 3. Crystal structure of **3** as viewed perpendicular (top) and parallel to the {Co₈} plane. Hydrogen atoms have been omitted for clarity.

The core in **3** comprises a near planar array of Co(II) centres and its inorganic core may be described as comprising six edge-sharing $[\text{Co}(\text{II})_3]$ triangles or alternatively as comprising six vertex-sharing partial $[\text{Co}_3\text{O}_4]$ cubes (Fig. 4). The cobalt oxidation states were again assigned from BVS calculations, charge balance and bond length assessments. Co3 and Co4 exhibit distorted trigonal bipyramidal ($\tau = 0.70$) and tetrahedral geometries respectively (although a fifth close contact exists between Co4 and O13: $\text{Co4}\cdots\text{O13} = 2.595 \text{ \AA}$), while Co1 and Co2 possess distorted octahedral geometries. The Co(II) centres in **3** are connected *via* a combination of μ_3 -bridging OMe^- (O57 and s.e) and two crystallographically unique $\eta^1:\eta^3, \mu_3$ -2-hp $^-$ ions (N15 and O13 and N8 and O6, respectively) and $\eta^2:\eta^2, \mu_3$ -bridging 2,2'-biphenolate ligands (*via* the O_{phen} atoms O2, O30, O4 and O17). More specifically the OMe^- ions sit above and below the $\{\text{Co}(\text{II})_8\}$ plane respectively, connecting the central Co1 and Co2 ions with their symmetry equivalents. Likewise the bridging 2-hp $^-$ ligands sit above and below the planar octametallate core, terminally bonding to the tetrahedral Co3 and Co4 ions (via N8 and N15 respectively), while linking the more central Co1 and Co2 (and s.e) centres. Unlike all the other bridging ligands in **3** the 2,2'-biphenolate ligands sit approximately parallel to the $\{\text{Co}(\text{II})_8\}$ plane, lying along the edges of the complex as they bridge three Co(II) centres (Fig. 3). The coordination spheres at the metal centres are completed by terminal MeCN ligands at Co2 and Co3 ($\text{Co2-N59} = 2.144 \text{ \AA}$, $\text{Co3-N62} = 2.016 \text{ \AA}$), while terminally bonded singly deprotonated 2,2'-biphenolate ligands (O43) occupy the 4th coordination sites at Co4 (and s.e). Note that these ligands (LH^-) are disordered over two sites and modelled accordingly (see experimental section for details).

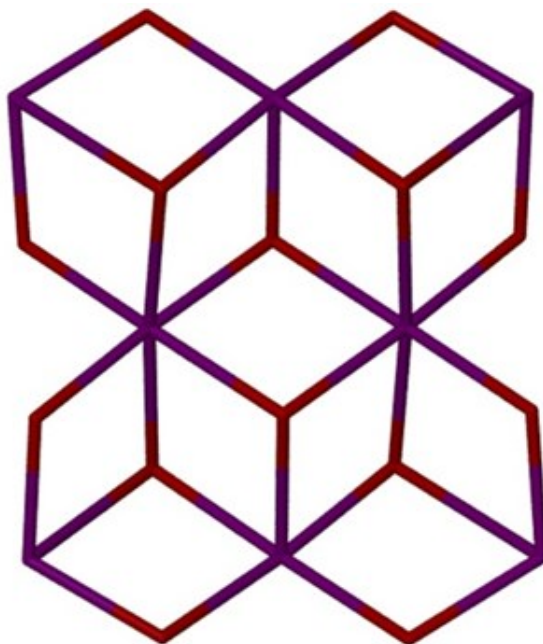


Figure 4. Inorganic core in **3** highlighting the six face sharing $\{\text{Co}(\text{II})_3\text{O}\}$ triangular units that make up the structure. *Note:* Can also be described as comprising six vertex-sharing partial $[\text{Co}_3\text{O}_4]$ cubes.

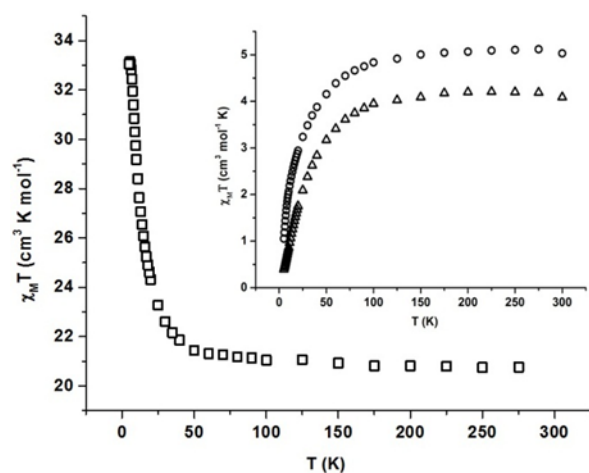
	1.2EtOH	2	3.MeCN	4
Formula ^a	C ₄₈ H ₄₈ N ₄ O ₆ Co ₂	C ₇₂ H ₆₄ N ₄ O ₈ Co ₂	C ₁₀₄ H ₈₇ N ₉ O ₁₈ Co ₈	C ₅₀ H ₄₇ N ₅ O ₇ Co ₁
M _w	894.76	1231.13	2222.35	888.86
Crystal System	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P2 ₁ /n	Pc
a/Å	10.416(2)	11.119(2)	12.7876(5)	10.572(2)
b/Å	11.022(2)	12.486(3)	19.4297(7)	13.755(3)
c/Å	11.536(2)	13.342(3)	20.1892(8)	15.127(3)
α/°	114.31(3)	111.49(3)	90	90
β/°	92.94(3)	113.74(3)	103.649(4)	94.03(3)
γ/°	115.71(3)	113.74(3)	90	90
V/Å ³	1043.9(4)	1512.3(5)	4874.5(3)	2194.2(8)
Z	1	1	2	2
T/K	150(2)	150(2)	150(2)	150(2)
λ ^b /Å	0.7107	0.7107	0.7107	0.7107
D _c /g cm ⁻³	1.423	1.352	1.514	2.345
μ(Mo-Kα)/ mm ⁻¹	0.850	0.610	1.399	0.450
Meas./indep.(R _{int}) refl.	3814 / 3510 (0.0154)	5527 / 4451 (0.0239)	11257 / 6831 (0.0472)	5134 / 3308 (0.0860)
Restraints, Parameters	0, 248	0, 389	475, 557	2, 571
wR2 (all data)	0.0875	0.0811	0.0232	0.1542
R1 ^{d,e}	0.0347	0.0337	0.0698	0.0736
Goodness of fit on F ²	1.042	1.018	1.116	1.027

Table 1. Crystallographic data for complexes **1-4**

Magnetic susceptibility measurements

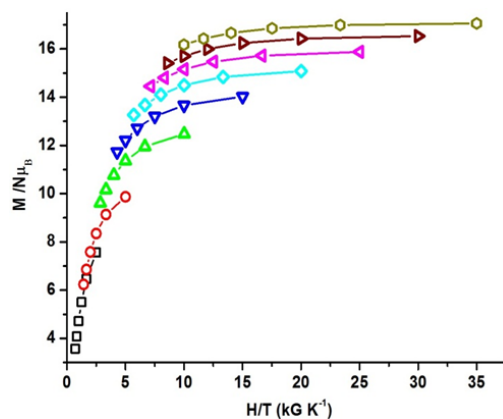
Magnetic measurements were carried out on polycrystalline samples of **1-3** in the 300-5 K temperature range and an external field of 0.1 T (Fig. 5). The room temperature $\chi_M T$ products for **1** and **2** are both consistent with that expected for two non interacting $s = 3/2$ ions with anisotropic g -values. On decreasing temperature their magnetic susceptibilities decrease slowly down to ~100 K, after which a more significant drop in their $\chi_M T$ products is observed, to minimum values of 0.4 and 1.05 cm³ K mol⁻¹, respectively. This behaviour is consistent with antiferromagnetic exchange and diamagnetic ground states in both. Indeed the rather obtuse Co-OR-Co angles of 103.5° in **1** and

103.33° in **2** would be expected to mediate AF exchange.¹² The behaviour of **3** is however quite different. The $\chi_M T$ value at 300 K (20.76 cm³ K mol⁻¹) is consistent with that expected for eight non interacting Co(II) centres (19.80 cm³ K mol⁻¹), assuming $s = 3/2$ and $g \sim 2.3$. As shown in Figure 5, $\chi_M T$ rises gradually down to a temperature of approximately 50 K before sharply increasing to a maximum of ~ 33 cm³ K mol⁻¹ at 5 K. This is clearly indicative of ferromagnetic exchange, and is corroborated by a Curie-Weiss analysis of the $1/\chi$ vs. T data which affords $\theta = +2.75$ K (Fig. S3). Magnetisation measurements in the 2-7 K temperature range in external fields ranging from 0.5 – 7 T were then obtained (Fig. 6). The saturation value of $M/N\mu_B$ of ~ 17.05 is consistent with an effective $S' = 4$ ground spin state originating from the weak ferromagnetic coupling of eight Co(II) ions each possessing an effective $s' = 1/2$ and assuming $g \sim 4.3$. Such magnetic exchange is perhaps to be expected for **3** when one considers the metal-oxygen core to be constructed from [M₃O₄] partial cubanes (M(II) cubes are invariably ferromagnetic).¹³ Moreover its structure is similar to the complex [Co(III)Co(II)₆(thme)₂(O₂CMe₃)₈Br₂].MeCN]¹² and even more similar to [Ni(II)₈(thme)₂(O₂CPh)₄Cl₆(MeCN)₆(H₂O)₂]¹⁴ (where H₃thme = 1,1,1'-tris(hydroxymethyl)ethane), both of which display ferromagnetic exchange.



← **Figure 5.** Plots of $\chi_M T$ vs. T obtained from polycrystalline samples of **3** (□) in the 300-5 K temperature range in an applied field of 0.1 T. Inset: Overlay of $\chi_M T$ vs. T data obtained from **1** (O) and **2** (Δ) measured under the same conditions.

Figure 6. → Plot of $M/N\mu_B$ vs H/T (kG K⁻¹) obtained on a polycrystalline complex of **3** in external magnetic fields of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7 T in the 7-2 K temperature range.



In order to deliberately engineer an extended architecture and expand the coordination chemistry of the 2,2'-biphenol ligand, the ditopic dipyridyl ligand 4,4'-trimethylenedipyridine (4,4'-tmdp) was introduced into the Co(II) / LH₂ / base synthon used previously in the production of **1-3**. The result was the formation of {[Co(II)(LH)(4,4'-tmdp)₂(NO₃)](LH₂)}_n (**4**): a 1D coordination polymer comprising both bridging and book-end 2,2'-biphenol moieties. **4** crystallises in the monoclinic *Pc* space group with an asymmetric unit comprising a distorted octahedral Co(II) centre connected to two independent 4,4'-tmdp ligands (*via* N1 and N2 respectively with distances Co1-N1 = 2.141 Å, Co1-N2 = 2.113 Å); one singly deprotonated terminally bound LH⁻ ligand (O1) and one chelating NO₃⁻ anion (O3 and O4). The last coordination spot (not part of the a.s.u) is occupied by another linear connector 4,4'-tmdp ligand (N4') (Fig. S4). The singly deprotonated LH⁻ ligand possesses an intramolecular H-bond between its O_{phen} donor and acceptor atoms (O2(H2H)⋯O1 = 1.692 Å). The neutral 2,2'-biphenol ligand (LH₂) lies at the pendant end of one of the 4,4'-tmdp ligands and is held in this position *via* H-bonds between its O_{phen} proton (H6) and the juxtaposed N-donor atom N5 to give a distance of O6(H6)⋯N5 = 1.958 Å. Moreover this same LH₂ unit (as observed previously in **2**) exhibits an intramolecular H-bond to nearby O_{phen} donor and acceptor atoms (O7(H7)⋯O6 = 1.826 Å).

The extended structure in **4** is best described as centering on a backbone of Co(II) chains which are propagated by covalently bonded 4,4'-tmdp ligands. These ligands alternate in their relative orientation to give a wave-like shape along the chains (Fig. 7a). The singly occupied LH⁻ ligands in **4** also alternate their relative orientation with respect to one another along the 1D [Co(II)-(4,4'-tmdp)-Co(II)-]_n rows, which is best observed in Figure 7c. As briefly mentioned earlier the second type of 4,4'-tmdp ligand in the a.s.u. bonds to Co1 (and s.e) at just one N-donor site (N2) which leaves the second N centre (N5) to interact with the aforementioned pendant LH₂ unit. Interestingly these pendant arms possess an arc shape and alternate in their direction as they propagate away from the Co(II) centres to form a *hemi ribcage* type structure (where the covalent Co(II) chain is the backbone and the pendant arms are the ribs) (Figs. 7 and 8). These rows of *rib-cage* like structures then stack in an off-set parallel manner on top of one another as highlighted in Figure 8; interacting *via* C-H⋯π interactions between the 4,4'-tmdp aromatic protons (H10) and nearby LH⁻ aromatic rings (C33-C38) at a distance of C10(H10)⋯π = 2.762 Å. Each *hemi ribcage* unit shows alternating phases with respect to their wave-like Co(II) backbone and pendant arm ribs. These stacked 1D chains arrange in parallel rows along the *b* cell direction to complete 3D connectivity in **4** and are linked *via* H-bonds between individual LH₂ units of adjacent *rib-cage* units (i.e. C46(H46)⋯O2 = 2.332 Å).

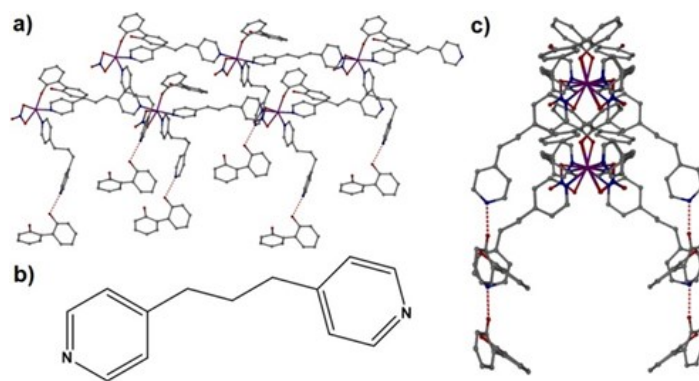


Figure 7. Packing in **4** showing the arrangement of two independent $[-Co(II)-(4,4'-tmdp)]_n$ chains as viewed perpendicular (a) and parallel (c) to their linear structures. Dashed red lines represent H-bonding as described in the text. (b) ChemDraw representation of the 4,4'-trimethylenedipyridine (4,4'-tmdp) ligand.

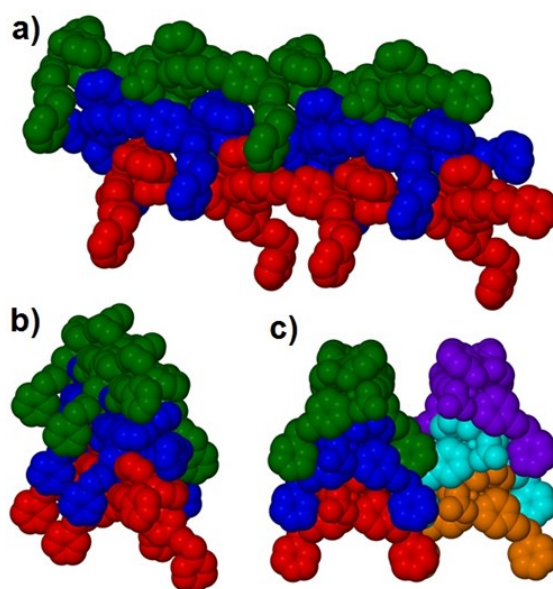


Figure 8. Space-fill representations of the separate 1D chains in **4** (distinguished *via* different colours) as viewed perpendicular (a) and along the chain directions (b and c). The pendant LH_2 ligands have been omitted for clarity.

Further investigations into the introduction of other dipyriddy ligands led to the use of *trans*-1,2-bis(4-dipyriddy)ethylene (*trans*-bpe). Various bench top reactions performed under ambient conditions, involving numerous combinations of $Co(II)$ / LH_2 / *trans*-bpe / base mixtures gave no isolable/discernable products. It was therefore decided to employ forcing conditions by performing the reaction in a microwave reactor (see experimental section for details), which gave almost

immediate success. $\text{Co(II)NO}_3 \cdot 6\text{H}_2\text{O}$, LH₂ and trans-bpe (1:1:1 ratio) were dissolved in a MeOH / MeCN solvent mixture (50/50) and stirred for 2 minutes before being placed in the microwave reactor for 5 minutes (at 200 W power) at a temperature and pressure of 160° C and 300psi, respectively. The resultant pink mother liquor was filtered and crystals of $[\text{Co(II)(LH)(trans-bpe)}_{1.5}(\text{NO}_3)]_n$ (**5**) were soon obtained after slow evaporation.

The asymmetric unit in **5** comprises a solitary Co(II) centre (Co1) bound to one singly deprotonated LH⁻ ligand (O1: Co1-O1 = 1.982 Å) which exhibits (as in **4**) an intramolecular H-bond at a distance of O2(H2H)⋯O1 = 1.656 Å. This Co(II) centre is also chelated by a NO₃⁻ anion along with three terminally bonded 1,2-trans(4-bipyridyl)ethylene ligands, although only half of each ligand appears in the asymmetric unit (Fig. 9a). These three dipyriddy ligands act as ditopic linkers to the individual {Co(II)(LH)(NO₃)} nodes, which are T-shaped in nature and the result is a 2D brickwork lattice topology (Fig. 9b). These individual sheets dissect the *ac* plane of the unit cell and stack in a parallel but staggered and interdigitated arrangement along the *b* cell direction. Interestingly the 2D sheets alternate in their relative orientations whereby the T-shaped nodes on adjacent sheets lie at right angles to one another (Fig. 10a cf. 10b).

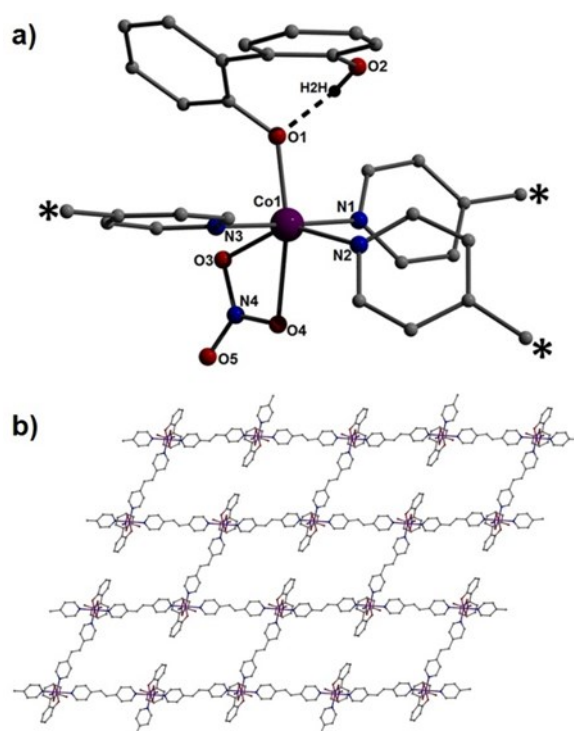


Figure 9. (a) Asymmetric unit in **5**. The * symbols represent the three propagation points at the nodes in **5**. The dashed lines represent the intramolecular hydrogen bond: O2(H2H)⋯O1 = 1.657 Å. (b) A 2D sheet of **5** showing a brickwork motif.

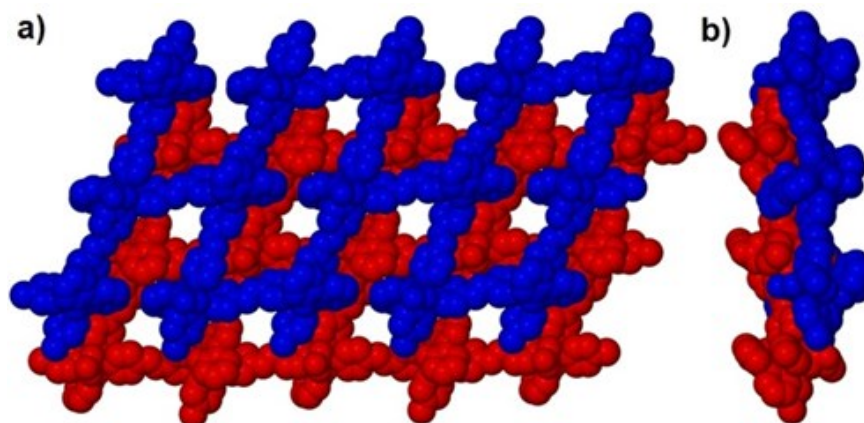


Figure 10. Two adjacent colour coded space-fill represented brickwork sheets in **5** as viewed perpendicular (a) and parallel (b) to the 2D plane.

Conclusions

We have shown that 2,2'-biphenol is an extremely versatile ligand which, when coupled with the correct co-ligand, will result in the production of magnetically interesting discrete polynuclear clusters or magnetically dilute extended network materials. Complex **3** represents the second largest cluster to be produced using this ligand, while the production of **4** and **5** represent rare examples of coordination polymers⁷ constructed using this ligand. Indeed they are the first to be built with Co(II) nodes. We are currently working towards expanding upon these initial findings, to include heterometallic 3d complexes, as well as the incorporation of Ln(III) ions.

Experimental Section

Infra-red spectra were recorded on a Perkin Elmer FT-IR *Spectrum One* spectrometer equipped with a Universal ATR Sampling accessory (NUI Galway). UV-visible studies were carried out on a Cary *100 Scan* (Varian) spectrophotometer. Elemental analysis was carried at the School of Chemistry microanalysis service at NUI Galway. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.8 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. The synthesis of **5** was carried out in a CEM Discovery microwave reactor.

Crystal structure information

The structures of **1-5** were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)¹⁵ and refined by full matrix least squares using SHELXL-97.¹⁶ SHELX operations were automated using the OSCAIL software package.¹⁷ All hydrogen atoms in **1-5** were assigned to idealised positions. The two crystallographically related 2,2'-biphenolate (LH⁻) ligands in **3** exhibited disorder and so were modelled isotropically over two sites in 50:50 occupancy. This was carried out using the CRYSTALS program at the University of Edinburgh (AP). Rigid restraints were also imposed on the aromatic rings of these ligands.

Syntheses

All reagents and solvents were used as purchased. *Caution:* Although no problems were encountered in this work, care should be taken when manipulating the potentially explosive nitrate salts.

Synthesis of [Co(II)(L)₂(py)₄].2EtOH (1): Co(NO₃)₂.6H₂O (0.5 g, 1.7 mmol) and 2,2'-biphenol (0.64 g, 3.4 mmol) were dissolved in 40 cm³ EtOH. 1 cm³ of a 40% aqueous solution of NEt₄OH was added slowly, resulting in a colour change from red to purple. The solution was stirred for 5 minutes, after which time pyridine (1 cm³, 12.4 mmol) was added. The solution was left stirring for a further 5 minutes, filtered and allowed to stand in a fume-cupboard covered by a perforated lid. Purple X-ray quality crystals were obtained upon slow evaporation of the mother liquor in 20% yield. Elemental analysis calculated (found) for C₄₈H₄₈N₄O₆Co₂: C 64.43 (64.02), H 5.41 (5.15), N 6.26 (6.39). FT-IR (cm⁻¹): 3176.6 (w), 3058.1 (w), 2965.3 (w), 695.1 (vs), 2861.1 (w), 1600.1 (w), 1591.0 (w), 1551.8 (w), 1482.1 (m), 1467.7 (m), 1442.6 (m), 1428.7 (m), 1373.8 (w), 1277.3 (m), 1263.4 (m), 1246.1 (m), 1214.1 (w), 1152.3 (w), 1116.9 (w), 1094.3 (m), 1068.7 (w), 1052.8 (m), 1042.1 (m), 1034.8 (m), 1000.2 (w), 947.0 (w), 931.1 (w), 879.9 (w), 858.8 (m), 850.2 (m), 836.0 (m), 751.2 (s), 731.8 (m).

Synthesis of [Co(II)₂(L)₂(4-pic)₄].2(LH₂) (2): Co(NO₃)₂.6H₂O (0.5 g, 1.7 mmol) and 2,2'-biphenol (0.64 g, 3.4 mmol) were dissolved in 40 cm³ EtOH. NMe₄OH·4H₂O (0.31 g, 1.9 mmol) was added, followed by 4-picoline (2 cm³, 20.54 mmol) and the resultant deep purple solution stirred for 5 minutes. After this time the solution was filtered and allowed to stand in a fume-cupboard covered by a perforated lid. Purple X-ray quality crystals of **2** were obtained upon slow evaporation of the mother

liquor in 20% yield. Elemental analysis calculated (found) for $C_{72}H_{64}N_4O_8Co_2$: C 70.24 (69.93), H 5.24 (5.24), N 4.55 (4.47). FT-IR (cm^{-1}): 3054.8 (w), 1620.7 (m), 1593.9 (w), 1581.7 (w), 1563.3 (w), 1504.9 (w), 1483.4 (m), 1468.6 (m), 1429.2 (s), 1262.4 (m), 1223.3 (s), 1149.5 (w), 1114.6 (w), 1094.1 (w), 1066.2 (w), 1040.6 (w), 1019.0 (w), 1002.4 (w), 965.6 (w), 935.2 (w), 854.7 (m), 835.8 (m), 806.9 (m), 760.2 (vs), 748.8 (vs), 729.4 (s), 703.6 (m).

Synthesis of $[Co(II)_8(OMe)_2(L)_4(LH)_2(2-hp)_4(MeCN)_4].MeCN$ (3): $Co(NO_3)_2 \cdot 6H_2O$ (0.4 g, 1.37 mmol) and 2,2'-biphenol (0.51 g, 2.74 mmol) were dissolved in a 50:50 MeOH/MeCN solvent mix (40 cm^3 total volume). NaOH (0.11 g, 2.74 mmol) and 2-hydroxypyridine (0.39 g, 4.1 mmol) were added in quick succession and the resultant deep purple solution was stirred for 40 mins. After this time the solution was filtered and allowed to stand. Purple X-ray quality crystals of **3** were obtained upon slow evaporation of the mother liquor in 25% yield. Elemental analysis calculated (found) for $C_{104}H_{87}N_9O_{18}Co_8$: C 56.21 (56.55), H 3.95 (3.29), N 5.67 (5.81). FT-IR (cm^{-1}): 3013.1 (w), 2920.5 (w), 2819.4 (w), 2277.4 (w), 1644.4 (w), 1606.1 (s), 1557.2 (w), 1490.0 (m), 1471.9 (s), 1435.5 (vs), 1321.8 (m), 1276.7 (s), 1257.0 (m), 1234.5 (s), 1150.6 (w), 1118.2 (w), 1097.6 (w), 1019.1 (m), 1004.1 (w), 930.7 (w), 870.0 (m), 855.0 (m), 846.0 (m), 787.1 (m), 754.0 (vs), 729.7 (s), 707.7 (m).

Synthesis of $\{[Co(II)(LH)(4,4-tmdp)_2(NO_3)](LH_2)\}_n$ (4): $Co(NO_3)_2 \cdot 6H_2O$ (0.5 g, 1.7 mmol) and 2,2'-biphenol (0.64 g, 3.4 mmol) were dissolved in 40 cm^3 EtOH. 2 cm^3 of a 40% aqueous solution of NEt_4OH was added slowly resulting in a colour change from red to purple. This was quickly followed by the addition of 4,4'-trimethylenedipyridine (0.68 g, 3.4 mmol) and the solution was stirred for 15 minutes. After this time the solution was filtered and allowed to stand. Pink X-ray quality crystals of **4** were obtained upon slow evaporation of the mother liquor in 15% yield. Elemental analysis calculated (found) for $C_{50}H_{47}N_5O_7Co$: C 67.56 (67.51), H 5.33 (5.62), N 7.88 (8.01). FT-IR (cm^{-1}): 3060.0 (w), 2931.0 (w), 1614.6 (m), 1587.7 (w), 1559.5 (w), 1465.0 (s), 1424.7 (s), 1283.0 (s), 1223.9 (s), 1151.1 (w), 1097.3 (w), 1069.2 (m), 1044.0 (w), 1017.5 (m), 939.1 (w), 845.6 (m), 826.9 (m), 811.6 (m), 793.6 (m), 751.1 (vs), 724.7 (s), 701.1 (m).

Synthesis of $\{[Co(II)(LH)(4,4-trans-bpe)_{1.5}(NO_3)]\}_n$ (5): $Co(NO_3)_2 \cdot 6H_2O$ (0.40 g, 1.37 mmol), 2,2'-biphenol (0.26 g, 1.37 mmol), trans-1,2-bis(4-pyridyl)ethylene (0.25 g, 1.37 mmol) and NaOH (0.055 g, 1.37 mmol) were added to 30 cm^3 of a MeOH:MeCN (50:50) solvent mixture. The resultant solution was premixed for two minutes and then microwaved for five minutes at $160^\circ C$, at a power of 200W and a pressure of 300psi. The resultant pink solution was cooled to $50^\circ C$ and the precipitate was

filtered off. The solution was allowed to stand for 2 days, after which time pink X-ray quality crystals of **5** were obtained in 20% yield. Elemental analysis calculated (found) for $C_{30}H_{21}N_4O_5Co_1$: C 62.51 (62.42), H 3.67 (3.89), N 9.72 (9.39). FT-IR (cm^{-1}): 3057.1 (w), 2283.5 (w), 1712.7 (w), 1605.1 (s), 1489.4 (s), 1416.9 (s), 1276.8 (vs), 1231.0 (m), 1217.4(s), 1204.7 (m), 1152.8 (w), 1120.2 (w), 1097.2 (w), 1067.7 (m), 1016.1 (m), 960.9 (m), 826.9 (s), 808.9 (s), 750.7 (vs), 722.6 (s), 700.7 (m).

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