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The first coordination polymers constructed using the 2,2'-biphenol ligand are described along with their ionic supramolecular counterparts.

The construction of coordination polymers is a vibrant area of research with interest in such fields as conductivity,\textsuperscript{1} molecular magnetism (i.e. Single-Chain Magnets\textsuperscript{2} and Spin-crossover materials\textsuperscript{3}), photo-active polymers\textsuperscript{4} and dual-functional materials comprising a hybrid of such physical properties.\textsuperscript{5} In terms of the construction of paramagnetic polynuclear architectures, the ability of the alkoxy- and phenoxy- functional groups (R-OH; R = alkyl, aryl) to bridge multiple 1\textsuperscript{st} row transition metal centres means they are the most commonly incorporated reactive groups in ligand design within the field of molecular magnetism.\textsuperscript{6} With this in mind we report here on our initial findings into the coordination chemistry of the 2,2'-biphenol (biphen) ligand. With the notable exceptions of the high spin decanuclear (12 \textsuperscript{th} row transition metal chemistry of the 2,2'-biphenol (biphen) ligand,\textsuperscript{7} it can be argued that the 1\textsuperscript{st} row transition metal chemistry of the 2,2'-biphenol ligand (with the exception of Ti\textsuperscript{4\textsuperscript{+}})\textsuperscript{8} has not been fully explored,\textsuperscript{9} while its coordination chemistry with 2\textsuperscript{nd} and 3\textsuperscript{rd} row metals is even less explored.\textsuperscript{10}

We describe here the synthesis and characterisation of a family of 1-D Mn\textsuperscript{3\textsuperscript{+}} based polymers linked covalently and ionically via the 2,2'-biphenol ligand as well as through N-donor co-ligands such as pyridine and its derivatives. Supramolecular interactions in the form of strongly directional hydrogen bonds are also imperative in the formation of certain members of this family. Our first foray involved the reaction of Mn(ClO\textsubscript{4})\textsubscript{2}.6H\textsubscript{2}O and 2,2'-biphenol (4 eq.) followed by one equivalent of NaOH in ethanol. No distinguishable product was formed from this mixture however on addition of an excess of pyridine (1cm\textsuperscript{3}, 12 eq.) followed by slow evaporation of the resultant mother liquor, X-ray quality needle-like crystals of [Na\textsubscript{2}Mn\textsubscript{2}(biphen)\textsubscript{4}(py)\textsubscript{3}(EtOH)\textsubscript{2}]\textsubscript{n} (I) were obtained in 20 \textperthousand yield, crystallising in the triclinic P-1 space group (Fig. 1). The structure in I consists of zig-zag chains comprising alternate Na\textsuperscript{+} and Mn\textsuperscript{3\textsuperscript{+}} metal centres which are connected predominantly by doubly deprotonated 2,2'-biphenol ligands exhibiting the $\eta_2^\prime\eta_2^\prime\mu_3$-bonding motif. Indeed this alternating Na$^+$-TM-Na$^+$-TM 1-D motif is an extremely rare architectural arrangement.\textsuperscript{11} Bridging EtOH molecules also help construct the 1-D array by connecting Na1 to Mn1 and Na2 to Mn3 via O5 and O10 (and symmetry equivalents) respectively (Fig. 1). The two crystallographically unique Na$^+$ ions (Na1 and Na2) both exhibit distorted octahedral geometries (Na-O bonds ranging from 2.329-2.646 \AA). This coordination geometry is also observed for Mn1 and Mn3 whose Jahn-Teller elongated axes lie along the Mn1-O5 (and s.e) and Mn3-O10 (and s.e) vertices with distances of 2.364 and 2.323 \AA respectively. It should be noted that Bond Valence Sum (BVS) calculations were employed to confirm the Mn\textsuperscript{3\textsuperscript{+}} oxidation state assignments in I and all other members of this family (Table S12). The shorter equatorial Mn-O bonds at centres Mn1 and Mn3 originate from the 2,2'-biphenolate ligands and produce bond distances ranging from 1.898 to 1.907 \AA. The Mn2 (and s.e) metal centre is five coordinate and gives a calculated $\tau$ value of 0.51, thus lying in between ideal trigonal bipyramidal ($\tau = 1$) and square based pyramid ($\tau = 0$) geometry.\textsuperscript{12} The terminal pyridine ligands (via N2) occupy the axial locale (Mn2-N1 = 2.192 \AA). The coordination geometries at the Na$^+$ (Na1 and Na2) are also completed by terminal pyridine ligands to give the bond lengths Na1-N2 = 2.485 \AA and Na2-N3 = 2.505 \AA (Fig. 1). The one-dimensional chains in I run along the bc diagonal (0 1 1 line) and due to their close proximity, three unique intrachain C-H···π interactions further stabilize the 1-D chain via the aromatic protons H25, H30 and H53 (H25···π centroid = 2.913 \AA, H30···π centroid = 2.913 \AA, H53···π centroid = 2.768 \AA) (Fig. SI1). The chains assemble through two unique C-H···π intermolecular interactions (H25···π centroid = 2.907 \AA and H46···π centroid = 2.850 \AA)\textsuperscript{13} to create a layer running parallel to the bc plane (Fig. SI1 and SII).
Fig. 1 Crystal structures of the 1-D chains in 1 (top) and 2 (bottom). Dashed lines in 2 represent H-bonding interactions as described in the text. Hydrogen atoms omitted for clarity. Colour code: Purple (Mn), Yellow (Na), Red (O), Blue (N), Grey (C).

Attempts at replacing the terminal pyridine ligands in 1 with the very occasionally ditopic 4-cyanopyridine (4-cnp) ligand led to the formation of the 1-D chain \([\text{Na}(\text{BiphenH}_2)(\text{EtOH})_2(\text{H}_2\text{O})][\text{Mn}(\text{biphen})_2(\text{4-cnp})_2]_n\) (2). Although extremely similar in their building block make-up the polymers of 1 and 2 are structurally very different. As previously described the chains in \([\text{Na}_2\text{Mn}_2(\text{biphen})_4(\text{py})_3(\text{EtOH})_2]_n\) (1) are predominantly covalent in bonding character while the linear arrays in 2 are comprised of strongly directional hydrogen bonding interactions. \([\text{Na}(\text{BiphenH}_2)(\text{EtOH})_2(\text{H}_2\text{O})][\text{Mn}(\text{biphen})_2(\text{4-cnp})_2]_n\) (2) crystallizes in the monoclinic space group \(P2_1/n\) (Fig. SI9) while the asymmetric unit contains one anionic \(\{\text{Mn}(\text{biphen})_2(\text{4-cnp})_2\}^-\) monomeric unit (Fig. 1). The anionic \(\{\text{Mn}(\text{biphen})_2(\text{4-cnp})_2\}^-\) moiety possesses a Jahn-Teller axially elongated six coordinate Mn\(^{3+}\) ion at its core. The equatorial positions of the distorted octahedron are occupied by four oxygen atoms of two chelating doubly deprotonated 2,2'-biphenol ligands. As observed regularly in coordination chemistry, the two 4-cyanopyridine ligands occupy the axial positions coordinating terminally to the Mn\(^{3+}\) ion (Mn1) via their nitrogen atoms with bond lengths of Mn1-N1 = 2.372 Å and Mn1-N3 = 2.371 Å. As expected these bond lengths are significantly greater than the Mn-O biphen distances which range between 1.890 – 1.934 Å. A five coordinate Na\(^+\) ion (Na1) lies at the centre of the monomeric \(\{\text{Na}(\text{BiphenH}_2)(\text{EtOH})_2(\text{H}_2\text{O})\}\) unit in 2 which possesses an +1 charge and thus charge balances the anionic manganese monomer to form the neutral species. Two oxygen atoms of one neutral chelating 2,2’-biphenol ligand are ligated to the alkali metal ion (\(\eta_1',\eta_1'^{-}\)-mode). The Na-O\(_{\text{biphen}}\) bond lengths are Na1-O5 = 2.358 Å and Na1-O6 = 2.330 Å while the three remaining coordination sites are each occupied by two terminal ethanol ligands (bonding via O7 and O8) and a terminal water molecule (O9). These Na-O(ethanol) bond lengths are given as 2.324 Å (Na1-O7) and 2.335 Å (Na1-O8) while the Na1-O9 distance is shown to be 2.316 Å.

Within the crystal structure the two mononuclear units in 2 partake in strong H-bonding interactions to form the infinite 1-D arrays of alternating Mn\(^{3+}\) and Na\(^+\) units that propagate along [1 0 0] (Fig. 1). These assemblies arise due to intrachain H-bonding between the deprotonated 2,2’-biphenol oxygen atoms (O1-O4) of the \(\{\text{Mn}(\text{biphen})_2(\text{4-cnp})_2\}^-\) unit, and the protons belonging to the EtOH and H\(_2\)O terminal ligands around the sodium monomer. More specifically these H-bonding donor protons originate from the chelating protonated biphenH\(_2\) ligand (via H5A and H6A) and via the protons from the terminal EtOH (via O7(H7A)) and H\(_2\)O ligands (O9 in Fig. 1). These H-bond distances as depicted by dashed lines in Figure 1 are O1…H5A(O5) = 1.773 Å, O2…H7A(O7) = 1.863 Å, O3…H6A(O6) = 1.742 Å and O4…O9 = 2.748 Å. The H-bonding H atoms (H5-H8) in 2 were located in the difference map and restrained to no less than 0.85(1) Å from their corresponding O atoms (O5-O8) using the DFIX parameter. The chains in 2 are further connected through O-H…N hydrogen bonds via the terminal EtOH ligands (O8(H8A)) and the nitrile N atoms (N4”) of a nearby 4-cnp ligands (O8(H8A)…N4” = 2.302 Å). These interchain interactions create a 2-D layer parallel to the \(ac\) plane (Fig. 2a).

The replacement of the 4-cnp ligand with 3-
cyanopyridine (3-cnp) leads to the formation of \([\text{Na}_2\text{Mn}_2(\text{biphen})(3\text{-}cnp)_2(\text{EtOH})_2]_n\) (3) (Fig. 2b): a covalent 1-D chain structurally very similar to that of \([\text{Na}_2\text{Mn}_2(\text{biphen})(\text{py})(\text{EtOH})]_2\) (I). For comparative purposes the main bonding atoms in the crystal structure of 3 were labelled identically to that of I. Once again the asymmetric unit in 3 comprises three and two crystallographically unique Mn\(^{3+}\) (Mn1-3) and Na\(^{+}\) (Na1 and Na2) centres respectively (Fig. S13). These are connected into the 1-D topology via numerous bridging 2,2'-biphenol ligands in the same manner as previously seen in 1 (\(\eta^2\)-\(\eta^2\)-\(\mu_2\)-motif; Fig. 3 and SI4). Likewise the Mn2 (and s.e) metal centre is five coordinate with a calculated \(\tau\) value of 0.54 and therefore also lies midway between ideal trigonal bipyramidal (\(\tau = 1\)) and distorted square based pyramid. Geometry. Terminal EtOH solvent molecules and 3-cnp ligands complete the coordination spheres at the metal centres (Fig. 3). Indeed on close comparison of both structures it becomes clear that the only major difference between I and 3 lies at the Na\(^{+}\) centres (Na1 and Na2). In I each of the sodium metal ions are coordinated to one terminal pyridine ligand while in 3 all Na\(^{+}\) centres are instead coordinated to one EtOH moiety (Fig. 1(top) cf. Fig. 2b). The components in 3 have assembled to create a one-dimensional chain along the 1 -1 -1 line, while four unique intrachain C-H…π interactions further stabilize the chain. These distances represented by dashed lines in figure 2b are given as (Å): H13…\(\pi\)centroid = 2.740 Å, H33…\(\pi\)centroid = 2.974 Å, H3A…\(\pi\)centroid = 2.751 Å and H18…\(\pi\)centroid = 2.748 Å (Fig. 2b). The chains assemble through one unique C-H…π interactions to create a 2-D layer running parallel to the 1 -1 -1 plane (H29…\(\pi\)centroid = 2.968 Å) (Fig. 2b).

By using 3-picoline (3-Mepy) as a co-ligand we once again switch to anionic chain analogue of 2 in the form of \([\text{Na}(\text{biphenH}_2)](\text{EtOH})_2][\text{Mn}(\text{biphen})(3\text{-}Mepy)]_2\) (4) which crystallizes in the triclinic P-1 space group. As observed in 2 the \([\text{Na}(\text{biphenH}_2)](\text{EtOH})_2]\ and the [\text{Mn}(\text{biphen})(3\text{-}Mepy)]_2\] units in 4 have assembled to create a one-dimensional chain by means of strong O-H…O hydrogen bonds (O1’ - H5A(OS) = 1.697 Å, O2’ - H7A(OT) = 1.836 Å, O3’ - H6A(O6) = 1.674 Å and O4’ - H9A(OS) = 1.842 Å). As observed during the structural refinement of 2 the H-bonding hydrogen atoms in 4 (labelled H5-H9) were also located in the difference map and restrained to a suitable distance using the DFIX parameter (see ESI for details). Moreover, as observed in 2 a sole C-H…π edge-to-face interaction exists in between the individual 1-D rows in 4 (H54B…\(\pi\)centroid = 3.245 Å).

Each of the 2,2'-biphenol ligands aiding the construction of chains 1-4 exhibit a twisting with respect to their aromatic rings and are forced into such a configuration presumably due to steric effects. On close crystal structure inspection it becomes apparent that the optimum torsion angle forged by the two connected rings lie at an average of approximately 52° (range: 47.82-57.57°) (Fig. S15) regardless of which bonding motif is employed (\(\eta^1\)-\(\eta^2\)-\(\mu_2\)- or \(\eta^1\)-\(\eta^2\)-\(\mu_3\)-). Indeed such torsion angles are in line with previously reported Mn\(^{3+}\),7,8,10 Fe\(^{3+}\),90 Ti\(^{4+}\),17 Pt\(^{2+}\),18) and lanthanide (Yb\(^{3+}\), La\(^{3+}\))19 complexes. It should be noted here that although not observed in this work the 2,2'-biphenol ligand also exhibits a unidentate bonding motif the torsion angle is as expected rather more acute (~35°).108

This twisting conformation shown by the 2,2-biphenol ligand has also been observed by the structurally similar binaphthyl-2,2'-diolato ligand (a.k.a binaphthol) when incorporated into various polynuclear transition metal (e.g. Fe\(^{3+}\),16 Cr\(^{3+}\),16 Ti\(^{4+}\),17 Pt\(^{2+}\),18) and lanthanide (Yb\(^{3+}\), La\(^{3+}\))19 complexes. It should be noted here that although not observed in this work the 2,2'-biphenol ligand is also able to exhibit the \(\eta^1\)-\(\eta^1\)-\(\mu_2\)-motif as shown in the previously reported complex \([[\text{C}_6\text{H}_{12}\text{N}]]_2[\text{Fe(biphen)}]_2\text{EtOH}]^{19}\).

All members of this family of chains show three sharp resonances in the 1400-1500 cm\(^{-1}\) region as expected for aromatic, polycyclic and / or pyridine rich systems. All siblings also possess IR resonances within the 850-750 cm\(^{-1}\) range and are indicative of out-of-plane aromatic C-H stretching. The IR peaks at 2238 cm\(^{-1}\) in 2 and 2237 cm\(^{-1}\) in 3 are attributed to the C=\(\equiv\)N stretches of the 4- and 3-cyanopyridine ligands respectively.20

The ionics nature of the supramolecular chains in 1 and 4 means that they are readily soluble in MeOH, EtOH and MeCN. Uv-vis studies on both complexes in all three of these solvents give rise to very similar spectra (SI7 and SI8) highlighting absorptions...
centred around 205nm (π→π*), 240nm (π→π*) and 290nm (n→π*) due to the multiple aromatic groups present in both ionic chains 2 and 4.20

The ionic chains 2 and 4 are almost identical in terms of their intrachain M·M distances with Mn1·Na1 values of 5.256 and 5.251 Å respectively. These distances within the covalent chains of 2 and 3 are as expected much closer and lie between 3.142 - 3.339 Å in 1 and 3.075 – 3.294 Å in 3 respectively (see Table S1I). Both these intrachain M·M distance ranges render the Mn3+ ions in 1-4 as magnetically isolated or dilute. Attempts at growing suitable crystals of 1-4 towards single-crystal EPR measurements (towards ascertaining Mn3+ zfs parameters) are currently underway. Synthetic investigations into the reactivity of other 1st row and Ln3+ paramagnetic ions in the presence of this phenolic ligand are also ongoing and will be also be reported at a later date.

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Notes and References

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1 All reagents and solvents were purchased commercially and used as supplied. For experimental data and specific crystallographic refinement information see ESI.

Crystal data for 1: C67H59N3O10Na2Mn: M = 1222.3, Triclinic, space group P-1, a = 11.989(2), b = 12.513(3), c = 22.786(5) Å, α = 90º, β = 84.81(3), γ = 78.51(3), V = 2957.6(10) Å3, T = 150(2) K, Z = 2, Dc = 1.372 g cm−3, GoF: 0.96, 10822 reflections collected of which 6185 were unique (Rint = 0.0599), R1 = 0.1125, wR2 = 0.4112 (F2, all data). CCDC 807777. Crystal data for 2: C52H46N4O9NaMn: M = 948.86, Monoclinic, space group P21/n, a = 10.377(2), b = 21.331(4), c = 23.121(5) Å, α = 90.06(2), β = 115.49(3), γ = 78.121(5), V = 2957.6(10) Å3, T = 150(2) K, Z = 2, Dc = 1.291 g cm−3, GoF: 1.065, 9016 reflections collected of which 6299 were unique (Rint = 0.0610), R1 = 0.1225, wR2 = 0.1411 (F2, all data). CCDC 807778.


We discuss the synthesis and structural characterisation of a family of bimetallic alternating Na/Mn coordination and ionic polymers. These extended architectures are the first to be constructed using the 2,2'-biphenol ligand.