Alternating Bimetallic Na/Mn Covalent and Ionic Chains

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

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The construction of coordination polymers is a vibrant area of research with interest in such fields as conductivity,† molecular magnetism (i.e. Single-Chain Magnets† and Spin-crossover materials†), photo-active polymers§ and dual-functional materials comprising a hybrid of such physical properties.¶ 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 1st row transition metal centres means they are the most commonly incorporated reactive groups in ligand design within the field of molecular magnetism.© 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 ≤ S ≤ 14) siblings of general formulae [NMe 4][Mn10O4(biphen)4X12] (X = Cl¯ and Br¯) and [Mn(MeCN)4(H2O)2][NHEt3][Mn10O4(biphen)4Br12], along with the ferromagnetic dinuclear complex [NEt4][Mn3(biphen)2(biphen)(2,2-bipy)] (bipy = 2,2′-biphenol; 2,2-bipy = 2,2-bipyridine), it can be argued that the 1st row transition metal chemistry of the 2,2′-biphenol ligand (with the exception of Ti4+) has not been fully exploited,© while its coordination chemistry with 2nd and 3rd row metals is even less explored.©

We describe here the synthesis and characterisation of a family of 1-D Mn3+ 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(ClO4)2.6H2O 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 (1cm3, 12 eq.) followed by slow evaporation of the resultant mother liquor, X-ray quality crystals of [Na2Mn2(biphen)4(py)3(EtOH)2]n (1) were obtained in 20 % yield, crystallising in the triclinic P-1 space group (Fig. 1). The structure in 1 consists of zig-zag chains comprising alternate Na⁺ and Mn3⁺ metal centres which are connected predominantly by doubly deprotonated 2,2′-biphenol ligands exhibiting the η2:η2:µ3-bonding motif. Indeed this alternating Na⁺-Mn⁺-Na⁺-Mn⁺-1-D motif is an extremely rare architectural arrangement.© 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 Å). 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 Å respectively. It should be noted that Bond Valence Sum (BVS) calculations were employed to confirm the Mn3⁺ oxidation state assignments in 1 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 Å. The Mn2 (and s.e) metal centre is five coordinate and gives a calculated τ value of 0.51, thus lying in between ideal trigonal bipyramidal (τ = 1) and square based pyramid (τ = 0) geometry.© The terminal pyridine ligands (via N2) occupy the axial locale (Mn2-N1 = 2.192 Å). The coordination geometries at the Na⁺ (Na1 and Na2) are also 70

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 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 [Na(BiphenH₂)(EtOH)₂(H₂O)][Mn(biphen)₂(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 [Na₂Mn₂(biphen)₄(py)₃(EtOH)₂]ₙ (1) are predominantly covalent in bonding character while the linear arrays in 2 are comprised of strongly directional hydrogen bonding interactions. [Na(BiphenH₂)(EtOH)₂(H₂O)][Mn(biphen)₂(4-cnp)₂]ₙ (2) crystallizes in the monoclinic space group P2₁/n (Fig. SI9) while the asymmetric unit contains one anionic {Mn(biphen)₂(4-cnp)₂}⁻ and one cationic {Na(BiphenH₂)(EtOH)₂(H₂O)}⁺ monomeric unit (Fig. 1). The anionic {Mn(biphen)₂(4-cnp)₂}⁻ moiety possesses a Jahn-Teller axially elongated six coordinate Mn³⁺ 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 Mn³⁺ 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 [Na(BiphenH₂)(EtOH)₂(H₂O)]⁻ 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 (η¹,η¹'-µ-mode). The Na-O(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 Mn³⁺ 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 {Mn(biphen)₂(4-cnp)₂}⁻ unit, and the protons belonging to the EtOH and H₂O terminal ligands around the sodium monomer. More specifically these H-bonding donor protons originate from the chelating protonated biphenH₂ ligand (via H5A and H6A) and via the protons from the terminal EtOH (via O7(H7A)) and H₂O 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 replacement of the 4-cnp ligand with 3-
cyanopyridine (3-cnp) leads to the formation of [Na₃M₃(biphen)₄(3-cnp)₂(EtOH)₃] (3) (Fig. 2b): a covalent 1-D chain structurally very similar to that of [Na₂M₃(biphen)(py)(EtOH)]₁₀ (1). For comparative purposes the main bonding atoms in the crystal structure of 3 were labelled identically to that of 1. Once again the asymmetric unit in 3 comprises three and two crystallographically unique Mn³⁺ (Mn₁-3) and Na⁺ (Na₁ and Na₂) centres respectively (Fig. SI3). These are connected into the 1-D topology via numerous bridging 2,2′-biphenol ligands in the same manner as previously seen in 1 (η¹,η²,µ₂-motif; Fig. 3 and SI4). Likewise the Mn₂ (and s.c) metal centre is five coordinate with a calculated τ value of 0.54 and therefore also lies midway between ideal trigonal bipyramidal (τ = 1) and distorted square based pyramid (τ = 0) 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 1 and 3 lies at the Na⁺ centres (Na₁ and Na₂). In 1 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 2b are given as (Å): H13⋯πcentroid = 2.740 Å, H33⋯πcentroid = 2.974 Å and H30⋯πcentroid = 2.751 Å and H18⋯πcentroid = 2.748 Å. 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⋯πcentroid = 2.968 Å) (Fig. 2b).

By using 3-picoline (3-Mepy) as a co-ligand we once again switch to an infinite chain analogue of 2 in the form of [Na₃(biphenvH₂)(EtOH)]₃[Mn(biphen)(3-Mepy)]₂ (4) which crystallizes in the triclinic P-1 space group. As observed in 2 the [Na₃(biphenvH₂)(EtOH)]₃ and the [Mn(biphen)(3-Mepy)]₂ ionic units in 4 have assembled to create a one-dimensional chain by means of strong O-H⋯O hydrogen bonds (O1⋯H5A(O5) = 1.692 Å, O2⋯H7A(O7) = 1.838 Å, O3⋯H6A(O6) = 1.674 Å and O4⋯H9A(O9) = 1.842 Å) and C-H⋯π interactions (H36B⋯π = 2.903 Å) running along the a axis. 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⋯πcentroid = 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. SI5) regardless of which bonding motif is employed (η¹,η²,µ₂- or η³,η²-µ₂-). Indeed such torsion angles are in line with previously reported Mn³⁺,7,8,10 Fe⁴⁺,10b Ti⁴⁺,9 and Rh²⁺ (ref. 11) transition metal complexes constructed using this ligand. We should also highlight that when 2,2-biphenol exhibits a unidentate bonding motif the torsion angle is as expected rather more acute (~35°).10b

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. Fe³⁺,16 Cr³⁺,16 Ti⁴⁺,17 Pt²⁺,18) and lanthanide (Yb³⁺, La³⁺)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 η³,η²-µ₂-bonding motif as shown in the previously reported complex [(C₅H₁₂N]₂[Fe(biphenvH₂)]₂EtOH].10b

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=N stretches of the 4- and 3-cyanopyridine ligands respectively.20 Theionic 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 S1). Both these intrachain M–M distances range 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 novel ligand are also ongoing and will be also be reported at a later date.

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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.