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Title	Alternating bimetallic Na/Mn covalent and ionic chains
Author(s)	Berg, Nelly; Jones, Leigh F.
Publication Date	2010-07-30
Publication Information	Berg, N, Jones, LF (2010) 'Alternating bimetallic Na/Mn covalent and ionic chains'. Crystengcomm, 12 :3518-3521.
Publisher	RSC
Link to publisher's version	http://dx.doi.org/10.1039/C0CE00218F
Item record	http://hdl.handle.net/10379/3868
DOI	http://dx.doi.org/DOI 10.1039/c0ce00218f

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Alternating Bimetallic Na/Mn Covalent and Ionic Chains

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Receipt/Acceptance Data [DO NOT ALTER/DELETE THIS TEXT]

Publication data [DO NOT ALTER/DELETE THIS TEXT]

DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

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,¹ molecular magnetism (i.e. Single-Chain Magnets² and Spin-crossover materials³), photo-active polymers⁴ and dual-functional materials comprising a hybrid of such physical properties.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 1st row transition metal centres means they are the most commonly incorporated reactive groups in ligand design within the field of molecular magnetism.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 ≤ S ≤ 14) siblings of general formulae [NMe₄]₄[Mn₁₀O₄(biphen)₄X₁₂] (X = Cl⁻ and Br⁻) and [Mn(MeCN)₄(H₂O)₂][NHEt₃][Mn₁₀O₄(biphen)₄Br₁₂],⁷ along with the ferromagnetic dinuclear complex [NEtH]₂[Mn₂(biphen)₂(biphenH)(2,2-bipy)] (biphen = 2,2'-biphenol; 2,2-bipy = 2,2-bipyridine),⁸ it can be argued that the 1st row transition metal chemistry of the 2,2'-biphenol ligand (with the exception of Ti⁴⁺)⁹ has not been fully exploited,¹⁰ while its coordination chemistry with 2nd and 3rd row metals is even less explored.¹¹

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 (1 cm³, 12 eq.) followed by slow evaporation of the resultant mother liquor, X-ray quality needle-like 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⁺···TM···Na⁺···TM··· 1-D motif is an extremely rare architectural arrangement.¹² 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.¹³ 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 completed by terminal pyridine ligands to give the bond lengths Na1-N2 = 2.485 Å and Na2-N3 = 2.505 Å (Fig. 1). The one-dimensional chains in **1** 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} = 2.995 Å, H30···π_{centroid} = 2.913 Å, H53···π_{centroid} = 2.768 Å) (Fig. S11). The chains assemble through two unique C-H···π intermolecular interactions (H27···π_{centroid} = 2.907 Å and H46···π_{centroid} = 2.850 Å) to create a layer running parallel to the bc plane (Fig. S11 and S12).

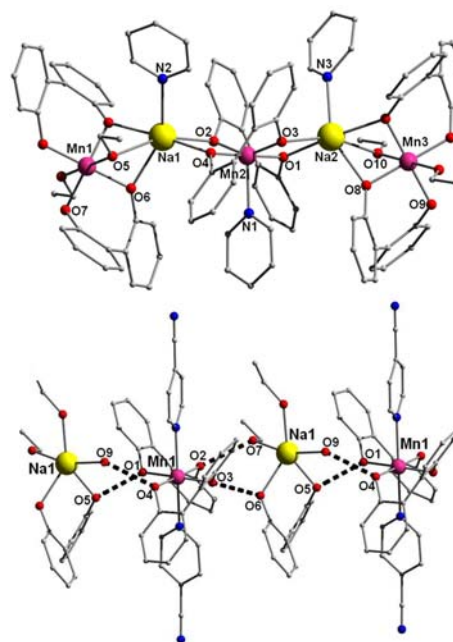


Fig. 1 Crystal structures of the 1-D chains in **1** (top) and **2** (bottom). Dashed lines in **2** represent H-bonding interactions as described in the text. Hydrogen atoms omitted for clarity. Colour code: Purple (Mn), Yellow (Na), Red (O), Blue (N), Grey (C).

Attempts at replacing the terminal pyridine ligands in **1** with the *very occasionally* ditopic 4-cyanopyridine (4-cnp)¹⁴ ligand led to the formation of the 1-D chain $[\text{Na}(\text{BiphenH}_2)(\text{EtOH})_2(\text{H}_2\text{O})][\text{Mn}(\text{biphen})_2(4\text{-cnp})_2]_n$ (**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. $[\text{Na}(\text{BiphenH}_2)(\text{EtOH})_2(\text{H}_2\text{O})][\text{Mn}(\text{biphen})_2(4\text{-cnp})_2]_n$ (**2**) crystallizes in the monoclinic space group $P2_1/n$ (Fig. S19) while the asymmetric unit contains one anionic $\{\text{Mn}(\text{biphen})_2(4\text{-cnp})_2\}^-$ and one cationic $\{\text{Na}(\text{BiphenH}_2)(\text{EtOH})_2(\text{H}_2\text{O})\}^+$ monomeric unit (Fig. 1). The anionic $\{\text{Mn}(\text{biphen})_2(4\text{-cnp})_2\}^-$ 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,¹⁵ 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 $\text{Mn1-N1} = 2.372 \text{ \AA}$ and $\text{Mn1-N3} = 2.371 \text{ \AA}$. As expected these bond lengths are significantly greater than the $\text{Mn-O}_{\text{biphen}}$ distances which range between $1.890 - 1.934 \text{ \AA}$. 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 ($\eta^1, \eta^1: \mu$ -mode). The $\text{Na-O}_{\text{biphen}}$ bond lengths are $\text{Na1-O5} = 2.358 \text{ \AA}$ and $\text{Na1-O6} = 2.330 \text{ \AA}$ 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 $\text{Na-O}(\text{ethanol})$ bond lengths are given as 2.324 \AA (Na1-O7) and 2.335 \AA (Na1-O8) while the Na1-O9 distance is shown to be 2.316 \AA .

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 $[100]$ (Fig. 1). These assemblies arise due to intrachain H-bonding between the deprotonated 2,2'-biphenol oxygen atoms (O1-O4) of the $\{\text{Mn}(\text{biphen})_2(4\text{-cnp})_2\}^-$ unit, and the protons belonging to the EtOH and H_2O 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 H_2O ligands (O9 in Fig. 1). These H-bond distances as depicted by dashed lines in Figure 1 are $\text{O1} \cdots \text{H5A}(\text{O5}) = 1.773 \text{ \AA}$, $\text{O2} \cdots \text{H7A}(\text{O7}) = 1.863 \text{ \AA}$, $\text{O3} \cdots \text{H6A}(\text{O6}) = 1.742 \text{ \AA}$ and $\text{O4} \cdots \text{O9} = 2.748 \text{ \AA}$. The H-bonding H atoms (H5-H8) in **2** were located in the difference map and restrained to no less than $0.85(1) \text{ \AA}$ from their corresponding O atoms (O5-O8) using the DFIX parameter. The chains in **2** are further connected through $\text{O-H} \cdots \text{N}$ hydrogen bonds via the terminal EtOH ligands (O8(H8A)) and the nitrile N atoms (N4'') of a nearby 4-cnp ligands ($(\text{O8})\text{H8A} \cdots \text{N4}'' = 2.302 \text{ \AA}$). These interchain interactions create a 2-D layer parallel to the *ac* plane (Fig. 2a).

The replacement of the 4-cnp ligand with 3-

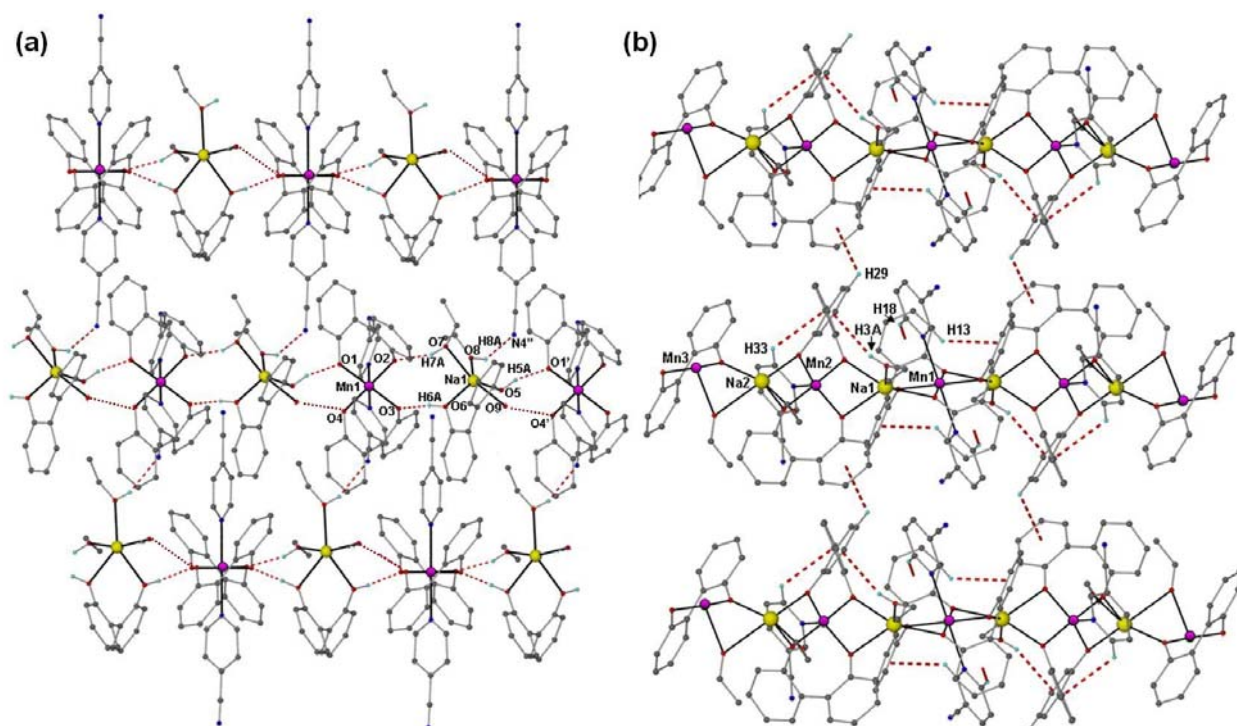


Fig. 2 The H-bonded chains in **2** (a) and covalent chains in **3** (b). The dashed lines represent both the intra- and interchain interactions within the **2** structures. Symmetry code (') in **2**: $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$. Colour code: Purple (Mn), Yellow (Na), Red (O), Blue (N), Grey (C) and Light blue (H).

cyanopyridine (3-cnp) leads to the formation of $[\text{Na}_2\text{Mn}_2(\text{biphen})_4(3\text{-cnp})_2(\text{EtOH})_3]$ (**3**) (Fig. 2b): a covalent 1-D

the structural refinement of **2** the H-bonding hydrogen atoms in **4** (labelled H5-H9) were also located in the difference map and

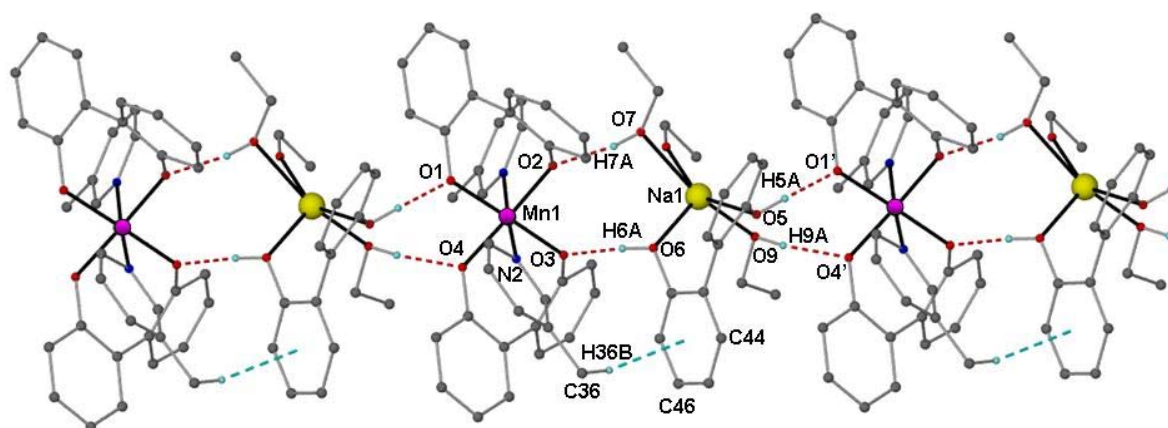


Fig. 3 The H-bonded chain along the *a* axis in **4**. All H atoms except those participating in supramolecular interactions have been removed for clarity. Symmetry code ($'$) $x-1, y, z$. Hydrogen bond distances (\AA): $\text{O1}\cdots\text{H5A}(\text{O5}) = 1.697 \text{ \AA}$, $\text{O2}\cdots\text{H7A}(\text{O7}) = 1.836 \text{ \AA}$, $\text{O3}\cdots\text{H6A}(\text{O6}) = 1.674 \text{ \AA}$ and $\text{O4}\cdots\text{H9A}(\text{O9}) = 1.842 \text{ \AA}$.

chain structurally very similar to that of $[\text{Na}_2\text{Mn}_2(\text{biphen})_4(\text{py})_3(\text{EtOH})_2]_n$ (**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 Mn^{3+} (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** ($\eta^2, \eta^2: \mu_3$ -motif; Fig. 3 and SI4). Likewise the Mn2 (and s.e) metal centre is five coordinate with a calculated τ value of 0.54 and therefore also lies midway between ideal trigonal bipyramidal ($\tau = 1$) and distorted square based pyramid ($\tau = 0$) 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 $\cdots\pi$ interactions further stabilize the chain. These distances represented by dashed lines in figure 2b are given as (\AA): $\text{H13}\cdots\pi_{\text{centroid}} = 2.740 \text{ \AA}$, $\text{H33}\cdots\pi_{\text{centroid}} = 2.974$, $\text{H3A}\cdots\pi_{\text{centroid}} = 2.751$ and $\text{H18}\cdots\pi_{\text{centroid}} = 2.748$. The chains assemble through one unique C-H $\cdots\pi$ interactions to create a 2-D layer running parallel to the 1 -1 -1 plane ($\text{H29}\cdots\pi_{\text{centroid}} = 2.968 \text{ \AA}$) (Fig. 2b).

By using 3-picoline (3-Mepy) as a co-ligand we once again switch to an ionic chain analogue of **2** in the form of $[\text{Na}(\text{biphenH}_2)(\text{EtOH})_3][\text{Mn}(\text{biphen})_2(3\text{-Mepy})_2]$ (**4**) which crystallizes in the triclinic P-1 space group. As observed in **2** the $[\text{Na}(\text{biphenH}_2)(\text{EtOH})_3]^+$ and the $[\text{Mn}(\text{biphen})_2(3\text{-Mepy})_2]^-$ ionic units in **4** have assembled to create a one-dimensional chain by means of strong O-H $\cdots\text{O}$ hydrogen bonds ($\text{O1}\cdots\text{H5A}(\text{O5}) = 1.692 \text{ \AA}$, $\text{O2}\cdots\text{H7A}(\text{O7}) = 1.838 \text{ \AA}$, $\text{O3}\cdots\text{H6A}(\text{O6}) = 1.674 \text{ \AA}$ and $\text{O4}\cdots\text{H9A}(\text{O9}) = 1.842 \text{ \AA}$) and C-H $\cdots\pi$ interactions ($\text{H36B}\cdots\pi_{\text{centroid}} = 2.903 \text{ \AA}$) running along the *a* axis. As observed during

restrained to a suitable distance using the DFIX parameter (see ESI for details). Moreover, as observed in **2** a sole C-H $\cdots\pi$ edge-to-face interaction exists in between the individual 1-D rows in **4** ($\text{H54B}\cdots\pi_{\text{centroid}} = 3.245 \text{ \AA}$).

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: $47.82\text{-}57.57^\circ$) (Fig. SI5) regardless of which bonding motif is employed ($\eta^2, \eta^2: \mu_3$ - or $\eta^1, \eta^1: \mu$ -). Indeed such torsion angles are in line with previously reported Mn^{3+} , 7,8,10 Fe^{3+} , 10a Ti^{4+} , 9 and Rh^{2+} (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 ($\sim 35^\circ$). 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. 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 $\eta^1, \eta^2: \mu_2$ -bonding motif as shown in the previously reported complex $[(\text{C}_5\text{H}_{12}\text{N})_2][\text{Fe}(\text{biphen})_4] \cdot 2\text{EtOH}$. 9a

All members of this family of chains show three sharp resonances in the $1400\text{-}1500 \text{ cm}^{-1}$ region as expected for aromatic, polycyclic and / or pyridine rich systems. All siblings also possess IR resonances within the $850\text{-}750 \text{ cm}^{-1}$ 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 ionic 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 ($\pi \rightarrow \pi^*$), 240nm ($\pi \rightarrow \pi^*$) and 290nm ($n \rightarrow \pi^*$) 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 M³⁺–M distances with Mn³⁺–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 S11). Both these intrachain M³⁺–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)²¹ 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.

Acknowledgements

The authors would like to thank the IRSCET Embark Program (NB) and the NUI Galway Millennium Fund (LFJ) for funding. The authors would also like to thank Prof. Patrick McArdle for crystallographic discussions contributing to this work.

Notes and References

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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**: C₆₇H₅₉N₃O₁₀Na₂Mn₂: M = 1222.3, Triclinic, space group P-1, a = 11.814(2), b = 12.513(3), c = 22.786(5) Å, α = 96.06(3), β = 98.11(3), γ = 115.49(3)°, V = 2957.6(10) Å³, T = 150(2) K, Z = 2, D_c = 1.372 g cm⁻³, GooF: 0.966, 10822 reflections collected of which 6185 were unique (R_{int} = 0.0599), R1 [I > 2σ(I)] = 0.1225, wR2 = 0.1411 (F₂, all data). **CCDC XXXXX**. 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, β = 99.53(3), γ = 90°, V = 5047.4(18) Å³, T = 150(2) K, Z = 4, D_c = 1.249 g cm⁻³, GooF: 1.059, 9233 reflections collected of which 5854 were unique (R_{int} = 0.0725), R1 [I > 2σ(I)] = 0.1069, wR2 = 0.2652 (F₂, all data). **CCDC xxxxx**. Crystal data for **3**: C₆₆H₅₈Na₄O₁₁Na₂Mn₂: M = 1239.02, Triclinic, space group P-1, a = 11.293(2), b = 15.606(3), c = 17.596(4) Å, α = 84.81(3), β = 77.73(3), γ = 81.07(3)°, V = 2988.3(10) Å³, T = 150(2) K, Z = 2, D_c = 1.377 g cm⁻³, GooF: 1.036, 10920 reflections collected of which 5906 were unique (R_{int} = 0.0814), R1 [I > 2σ(I)] = 0.1366, wR2 = 0.1580 (F₂, all data). **CCDC xxxxx**. Crystal data for **4**: C₅₄H₅₈N₂O₉NaMn: M = 956.95, Triclinic, space group P-1, a = 10.350(2), b = 11.989(2), c = 21.671(4) Å, α = 86.90(3), β = 78.51(3), γ = 69.14(3)°, V = 2462.1(9) Å³, T = 150(2) K, Z = 2, D_c = 1.291 g cm⁻³, GooF: 1.065, 9016 reflections collected of which 6299 were unique (R_{int} = 0.0610), R1 [I > 2σ(I)] = 0.0941, wR2 = 0.1454 (F₂, all data). **CCDC xxxxx**.

1. (a) C. Janiak. *Dalton Trans.*, 2003, 2781-2804 and references herein. (b) P. Amo-Ochoa, O. Castillo, S. S. Alexandre, L. Welte, P. J. de Pablo, M. I. Rodríguez-Tapiador, J. Gomez-Herrero and F. Zamora. *Inorg. Chem.*, 2009, **48**, 7931-7936. (c) L. Welte, A. Calzolari, R. Di Felice, F. Zamora and J. Gomez-Herrero. *Nature Nanotech.*, 2010, **5**, 110-115.
2. (a) O. Kahn, Yu. Pey, M. Verdager, J. P. Renard and J. Sletten. *J. Am. Chem. Soc.*, 1988, **110**, 782-789. (b) C. Coulon, H. Miyasaka and R. Clérac., *Struct. and Bonding, Springer-Verlag (Berlin)*, 2006, 163-206 and references herein.

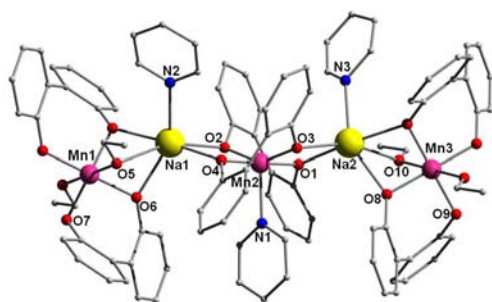
3. For examples see: (a) G. S. Matouzenko, G. Molnar, N. Bréfuel, M. Perrin, A. Bousseksou and S. A. Borshch., *Chem. Mater.*, 2003, **15**, 550-556. (b) C. Genre, G. S. Matouzenko, E. Jeanneau and D. Luneau. *New. J. Chem.*, 2006, **30**, 1669-1674. (c) S. M. Neville, B. A. Leita, D. A. Offermann, M. B. Duriska, B. Moubaraki, K. W. Chapman, G. J. Halder, K. S. Murray. *Eur. J. Inorg. Chem.*, 2007, 1073-1085.
4. (a) Z. Wang, Y.-H. Xing, C.-G. Wang, L.-X. Sun, J. Zhang, M.-F. Ge and Shu-Yun Niu., *CrystEngComm.*, 2010, **12**, 762-773. (b) C. Gao, S. Liu, L. Xie, Y. Ren, R. Cao, J. Cao and X. Zhao., *J. Mol. Struct.*, 2008, **891**, 384-387. (c) H. Adams, W. Z. Alsindi, G. M. Davies, M. B. Duriska, T. L. Easun, H. E. Fenton, J.-M. Herrera, M. W. George, K. L. Ronayne, X.-Z. Sun, M. Towrie and M. D. Ward., *Dalton Trans.*, 2006, 39 – 50.
5. (a) J. S. Galan-Mascaros and E. Coronado., *C. R. C. Chemie*, 2008, **116**, 1110-1116 and references herein. (b) E. Chelebaeva, J. Larionova, Y. Guari, R. A. Sa' Ferreira, L. D. Carlos, F. A. Almeida Paz, A. Trifonov, and C. Guerin., *Inorg. Chem.*, 2008, **47**, 775-777. (c) Z.-Y. Li, J.-W. Dai, N. Wang, H.-H. Qiu, S.-T. Yue and Y.-L. Liu., *Cryst. Growth. Des.*, 2010, DOI:10.1021/cg100245a. (d) S. Kitagawa, R. Kitaura and S.-i. Noro., *Angew. Chem. Int. Ed.*, 2004, **43**, 2334-2375 and references herein.
6. G. Aromi, E. K. Brechin., *Struct. and Bonding, Springer-Verlag (Berlin)*, 2006, 1-67 and references herein.
7. (a) D. P. Goldberg, A. Caneschi and S. J. Lippard., *J. Am. Chem. Soc.*, 1993, **115**, 9299-9300. (b) D. P. Goldberg, A. Caneschi, C. D. Delfs, R. Sessoli and S. J. Lippard. *J. Am. Chem. Soc.*, 1995, **117**, 5789-5800.
8. (a) A. R. Schake, E. A. Schmitt, A. J. Conti, W. E. Strieb, J. C. Huffman, D. N. Hendrickson and G. Christou., *Inorg. Chem.*, 1991, **30**, 3192-3199.
9. (a) J. P. Corden, W. Errington, P. Moore, M. G. Partridge and M. G. H. Wallbridge., *Dalton Trans.*, 2004, 1846-1851. (b) K. P. Bryliakov, D. E. Babushkin, E. P. Talsi, A. Z. Voskoboynikov, H. Gritzko, L. Schröder, H.-R. H. Damrau, U. Wieser, F. Schaper and H. Brintzinger., *Organometallics.*, 2005, **24**, 894-904. (c) T. A. Tsoeteti, A. Kuhn, A. Muller and J. Conradie., *Polyhedron.*, 2009, **28**, 209-214.
10. (a) E. W. Ainscough, A. M. Brodie and S. J. McLachlan., *J. Chem. Soc. Dalton Trans.*, 1983, 1385-1389. (b) J. S. Bashkin, A. N. Schake, J. B. Vincent, H.-R. Chang, Q. Li, J. C. Huffmann, G. Christou and D. N. Hendrickson., *J. Chem. Soc. Chem. Commun.*, 1988, 700-702.
11. (a) R. H. Laye, Z. R. Bell and M. D. Ward., *New J. Chem.*, 2003, **27**, 684-691. (b) H. Inoue, J.-I. Ito, M. Kikuchi and H. Nishiyama., *Chem. Asian J.*, 2008, **3**, 1284-1288.
12. (a) A. Saha, G. Musie and D. R. Powell., *Acta. Cryst.*, 2005, **E61**, m1144-m1146. (b) G.-H. Wang, Z.-G. Li, H.-Q. Jia, N.-H. Hu and J.-W. Xu., *Acta. Cryst.*, 2009, **C65**, m333-m336.
13. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor. *J. Chem. Soc., Dalton Trans.*, 1984, **7**, 1349-1356.
14. (a) D. T. Cromer and A. C. Larson., *Acta. Cryst.* 1972, **B28**, 1052. (b) W. Zhang, J. R. Jeitler, M. M. Turnbull, C. P. Landee, M. Wei and R. D. Willett., *Inorg. Chim. Acta.*, 1997, **256**, 183-198.
15. For examples see: (a) S. Dalai, P. S. Mukherjee, E. Zangrando and N. R. Chauduri., *New. J. Chem.*, 2002, **26**, 1185-1189. (b) S. Yoon and S. J. Lippard., *J. Am. Chem. Soc.*, 2005, **127**, 8386-8397. (c) B. Weber, C. Carbonera, C. Desplances and J.-F. Letard., *Eur. J. Inorg. Chem.*, 2008, 1589-1598.
16. R. J. Cross, L. C. Farrugia, D. R. McArthur, R. D. Peacock and D. S. C. Taylor., *Inorg. Chem.*, 1999, **38**, 5698-5702.
17. (a) K. M. Waltz, P. J. Carroll and P. J. Walsh., *Organometallics.*, 2004, **23**, 127-134.
18. (a) S. Doherty, C. R. Newman, R. K. Rath, J.-A. van der Berg, C. Hardacre, M. Nieuwenhuyzen and J. K. Knight., *Organometallics.*, 2004, **33**, 1055-1064. (b) N. M. Brunkan, P. S. White and M. R. Gagné., *Angew. Chem. Int. Ed.*, 1998, **37**, 1579-1582.

-
19. A. J. Wooton, P. J. Carroll and P. J. Walsh., *Org. Lett.*, 2007, **9**, 3359-3362. (b) Y. Horiuchi, V. Gnanadesikan, T. Ohshima, H. Masu, K. Katagiri, Y. Sei, K. Yamaguchi and M. Shibasaki., *Chem. Eur. J.*, 2005, **11**, 5195-5204.
20. D. H. Williams and I. Fleming., *Spectroscopic Methods in Organic Chemistry.*, McGraw-Hill. 1995, 5th Ed.
21. (a) S. J. W. Holgate, G. Bondarenko, D. Collison and F. E. Mabbs., *Inorg. Chem.*, 1999, **38**, 2380-2385. (b) S. Piligkos, D. Collison, V. S. Oganessian, G. Rajaraman, G. A. Timco, A. J. Thompson, R. E. P. Winpenny and E. J. L. McInnes., *Phys. Rev. B.*, 2004, **69**, 134424-134432. (c) S. Hill, S. Maccagnano, K. Park, R. M. Achey, J. M. North and N. S. Dalal., *Phys. Rev. B.*, 2002, **65**, 224410-224420. (d) R. Inglis, L. F. Jones, C. J. Milios, S. Datta, A. Collins, S. Parsons, W. Wernsdorfer, S. Hill, S. P. Perlepes, S. Piligkos, E. K. Brechin. *Dalton Trans.*, 2009, 3403-3412.

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TOC Entry



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'-
 100 biphenol ligand.

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