"Simple" oligopyridine complexes – sources of unexpected structural diversity

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Abstract

The simple formulae often presented for main-group metal complexes of oligopyridines (typically 2,2-bipyridine, 1,10-phenanthroline and 2,2':6',2"-terpyridine) hide a wide variety of polymeric solid-state structures. We present an overview of these structures and reveal a plethora of 1D chains, including ladder assemblies, and 2D networks. In most assemblies, the polymeric backbone or network is defined by the metal atoms and bridging ligands other than oligopyridines. The heterocyclic ligands typically feature as peripheral decorations, often engaging in face-to-face supramolecular π-stacking interactions which define the assembly of the crystal. In 1D coordination polymers, three types of decoration predominate which we have defined at Type 1 (all the oligopyridines on the same side and π-stacked, Type 2 (alternating arrangement of oligopyridines) and Type 3 (a pairwise alternating structure).

Introduction

This review is concerned with "simple" compounds formed between oligopyridine ligands and main group metal salts and it is an honour and a pleasure to acknowledge the enormous contributions that Allan White made to this area of chemistry. It is appropriate that this appears in the *Australian Journal of Chemistry*, not only because so much of Allan's own work was published in this journal, but also because Australia played a crucial role in the development of the chemistry of the oligopyridine ligands. The emphasis of the review is not on the exquisite and subtle details of geometry that so excited Allan, but rather upon the formation of coordination polymers and networks with a complexity greater than a simple formulation might indicate. This is also a fitting tribute to an area of chemistry that originated in Australia.[1]

37   The survey is limited to compounds of simple chelating oligopyridines and 1,10-
38   phenanthroline with inorganic anions and no additional ligands other than solvent. These
39   somewhat arbitrary criteria were selected for two reasons: firstly, the coordination chemistry
40   of the main group elements fascinated Allan in a world dominated by transition metal
41   chemists and, secondly, because the exclusion of other ligands allows a clear perception of
42   the underlying structural patterns and trends. We note that oligopyridines containing
43   additional donor capacity in substituents (typically carboxylate) are explicitly excluded.

44

Topology and dimensionality

46   Any discussion of coordination polymers and networks cannot avoid associated
47   forays into chemical topology and an understanding of the dimensionality of the systems.[2]
48   In this review, we use the terms 1D, 2D and 3D in a topologically strict sense. However, our
49   emphasis lies in the structural motifs developing from the metal centres, and in this
50   metallocentric and atomistic approach, the network representations given are
51   phenomenologically related to the "structure" rather than being based upon topologically
52   defined nodes (or virtual nodes). We apologize in advance to the topological purists. Part of
53   our motivation for this present work lies in a survey we recently published of early 2,2'-
54   bipyridine (bpy) complexes in which we showed that many of the "simple" transition metal
55   compounds $[MX_nL_p]$ (X = anion, L = oligopyridine) were actually coordination polymers.[3]

56   The survey of the compounds in this review leads to a general description of 1D, 2D
57   or 3D systems decorated with oligopyridines. Only in a very few cases do the oligopyridines
58   interact with more than one metal centre and play a role in the propagation of the polymer or
59   the network. Many of the compounds are 1D-coordination polymers and we introduce a
60   notation to describe the commonest types of decoration observed. In Type 1 (Fig. 1a) and
61   Type 2 (Fig. 1b) coordination polymers, the ligand decoration is arranged *up-up* or
62   alternating *up-down* with respect to the direction of propagation of the 1D chain. Less
63   commonly observed is Type 3 (Fig. 1c) with alternating *up-up-down-down* arrangements.
64   The 1D chain may be defined by mononuclear or polynuclear chemical repeat units in
65   network representations. In the case of Type 2 structures, the crystal packing is often defined
66   by an interdigitation of the polymer chains and face-to-face π-interactions between
67   oligopyridine ligands (Fig. 1d).

68   We have been guided by default covalent and ionic radii in the Cambridge Structural
69   Database (CSD)[4]for the identification of structures rather than the original authors'

70 descriptions. In main group chemistry, the debate "when is a bond not a bond" continues and
71 we note that one chemist's coordination polymer is another's weak interaction. *Caveat*
72 *emptor*. Finally, in a short apology to our colleagues in IUPAC, the kappa notation will not
73 be used rigorously; this is, in part because it is still a work in progress for complex
74 polynuclear systems, and in part because the extension to coordination networks is in its
75 infancy.
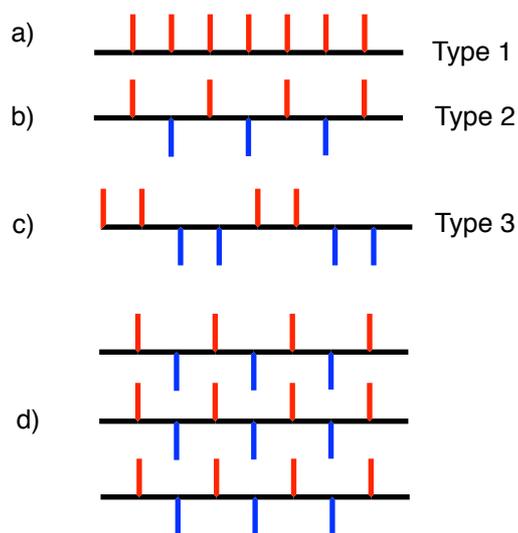
76
77 Figure 1 Three types of decoration of a 1D coordination polymer by oligopyridine ligands (a) all the
78 oligopyridines on the same side and π-stacked (*up-up*), (b) alternating arrangement of oligopyridines (*up-down*),
79 (c) a pairwise alternating structure (*up-up-down-down*), and (d) the typical packing of Type 2 polymers in the
80 lattice showing the π-stacking between adjacent chains.

81

Group 1 elements

83 Although many text-books suggest that the dominant coordination chemistry of the
84 group 1 metals is with oxygen donors, there is a large body of structural data relating to their
85 oligopyridine complexes. The commonest motif is a Type 2 1D polymer, although a number
86 of distinct structural types are known. The simplest Type 2 polymers with a linear chain
87 comprising mononuclear repeat units are found in $\{(2,9\text{-Me}_2\text{phen})\text{Li}(\mu\text{-NO}_3)\}_n$ (Fig. 2a),
88 $\{(2,9\text{-Me}_2\text{phen})\text{Li}(\mu\text{-NO}_3)\}_n$, $\{K(2,9\text{-Me}_2\text{phen})(\mu\text{-PF}_6)\}_n$ and $\{[\text{Na}(\text{phen})(\mu\text{-}$
89 $\text{OH}_2)_2]\text{I}\cdot\text{MeOH}\cdot\text{phen}\}_n$ which are obtained by reaction of the ligand and the appropriate salt
90 in methanol and in which a variety of bonding modes are exhibited by the bridging ligands.[5]
91 In $\{[\text{Na}(\text{phen})(\mu\text{-OH}_2)_2]\text{I}\cdot\text{MeOH}\cdot\text{phen}\}_n$, the "lattice" phen ligand is π-stacked with alternate
92 coordinated phen ligands (interplanar distance 3.44 Å) and also exhibits weak interactions
93 with the closest sodium ions (Na...N = 3.84, 4.70 Å for one Na^+ and 3.88, 4.92 Å for the
94 second Na^+). Type 2 polymers are also known with hetero- or homopolynuclear repeat units,

95 exemplified by $\{(Na(bpy)(OEt_2)[Mn(bpy)(CO)(\mu\text{-}CO)(\mu\text{-}CO)]\}_n,$[6] $\{Na(bpy)(\mu\text{-}ClO_4)\}_n,$[5]

96 $\{Na(phen)(\mu\text{-}BF_4)\}_n,$[7] and $\{Na(3,8\text{-}Br_2phen)(\mu\text{-}BF_4)\}_n,$[8] in which the decorating

97 oligopyridine ligands are flattened and tilted with respect to the propagation vector of the

98 polymer. Type 2 polymers are also known in which the repeat unit is polynuclear containing

99 metal centres not decorated with an oligopyridine. An example is the compound

100 $\{Li(bpy)I.LiI\}_n$ which is obtained from LiI–bpy melts and which comprises a Type 2 1D LiI

101 ladder with each Li in the rail capped by an iodine bridging two $\{Li(bpy)\}$ units (Fig. 2b).[9]

102 In contrast to $\{[Na(phen)(\mu\text{-}OH_2)_2]I\cdot MeOH\cdot phen\}_n,$ which is a Type 2 polymer,

103 $\{[Na(phen)(OH_2)_2(\mu\text{-}OH_2)_2]Br\cdot phen\}_n$ [10] exhibits a Type 3 arrangement of the decorating

104 ligands (Fig. 2c), also found in $\{[Na(bpy)(OH_2)][Cr(bpy)(CN)_2(\mu\text{-}CN)_2]\}_n.$[11] A single

105 example of a Type 1 polymer has been reported in the compound $\{Li(phen)(\mu\text{-}NO_3)\}_n$ (Fig.

106 2d) in which the decorating phen ligands are π-stacked with the next neighbour in the

107 chain.[12] In a classic paper, White showed that solvated and unsolvated compounds

108 $\{M(phen)_2X\}_n$ (M = Na, K, Rb; X = Br, I, PF$_6$, SCN) could be prepared in MeOH; all of the

109 compounds were 1D coordination polymers with no significant metal-anion contacts but a

110 wealth of differing binding modes for the phen, which generally interacted with two different

111 metal centres (a bonding mode for phen that is alien to the experience of most transition

112 metal chemists!).[13]

(a) (b)

(c) (d)
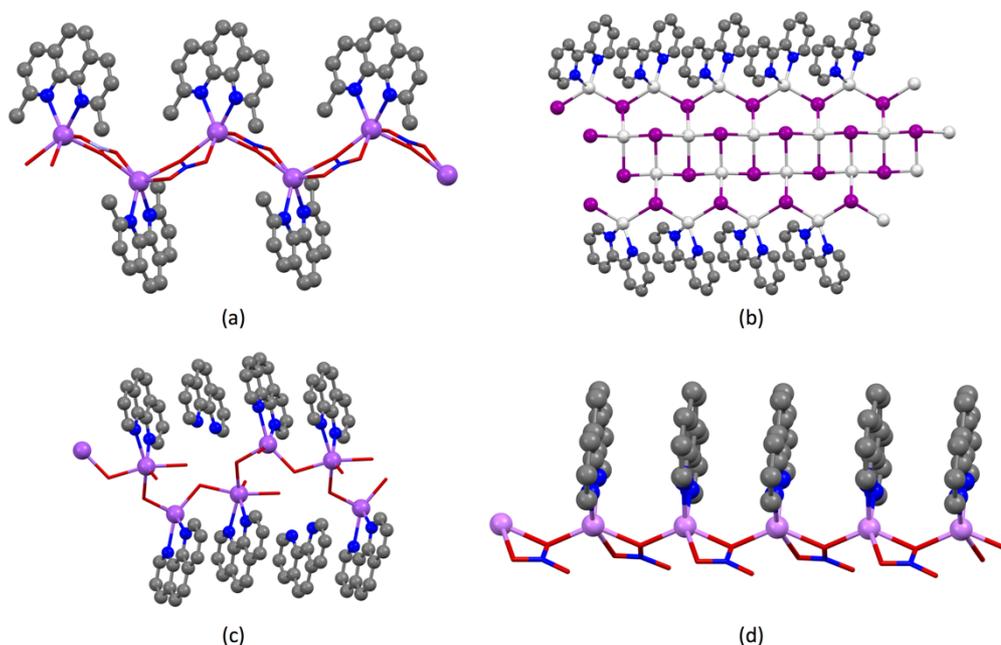
113

114 Figure 2. Polymers formed from group 1 elements exhibit various structures; (a) Type 2 mononuclear $\{(2,9\text{-}$

115 Me$_2$phen)Li(μ-NO$_3$)$\}_n$ (b) Type 2 polynuclear $\{Li(bpy)I.LiI\}_n$ (c) Type 3 $\{[Na(phen)(OH_2)_2(\mu\text{-}OH_2)_2]Br\cdot phen\}_n$

116 or (d) Type 1 $\{Li(phen)(\mu\text{-}NO_3)\}_n$. Hydrogen atoms have been omitted for clarity and structural elements other

117   than the oligopyridine and the metal(s) it is coordinated to are represented as capped sticks. Elements are
118   typically coloured with the standard CPK notation.

119

120   The remaining compounds of interest form 2D sheet structures in which the
121   decorating oligopyridine ligands lie above and below the plane described by the sheet. In the
122   complex $\{K(phen)_2[(OC)_5Cr(\mu\text{-}H)Cr(CO)_5]\}_n$ (Fig.   3a),   the $(OC)_5Cr(\mu\text{-}H)Cr(CO)_5$
123   coordination entity is coordinated to one potassium through three oxygen donors of one
124    $Cr(CO)_5$ moiety and to a second potassium by one oxygen of the second $Cr(CO)_5$ to generate
125   the 2D sheet.[14] A 2D structure is also observed in $\{K_2(phen)_2(Pt(CN)_4\}_n$, in which each
126    $Pt(CN)_4$ unit bridges two *trans* potassium ions through Pt-C-N-K interactions and a further
127   four potassiums by the remaining two cyanido ligands, each acting as a bridging nitrogen
128   donor. The end result is a sheet in which $K_2(\mu\text{-}CN)_2$ units are bridged by the $[Pt(CN)_4]^{2-}$
129   anions and capped top and bottom with phen ligands (Fig. 3b).[15] Dicyanidoaurate(1−) anions
130   have proved popular and a number of 2D structures with oligopyridine and group 1 metal
131   centres have been obtained. In $\{K(phen)Au(CN)_2\}_n$ and $\{K(bpy)Au(CN)_2\}_n$ (for which a
132   preliminary structure was reported in 1939[16]), each cyanido ligand in each $Au(CN)_2$
133   coordination entity acts as a bridging nitrogen donor to two potassium ions. In
134    $\{K(phen)Au(CN)_2\}_n$, pairs of potassium ions are also linked by a bridging phen ligand (Fig.
135   3c).[17] $\{K(bpy)Au(CN)_2\}_n$ possesses a similar structure, although the nature of the bridging
136   bpy ligand is, perhaps, less well defined.[17,18]

(a)   (b)

(c)
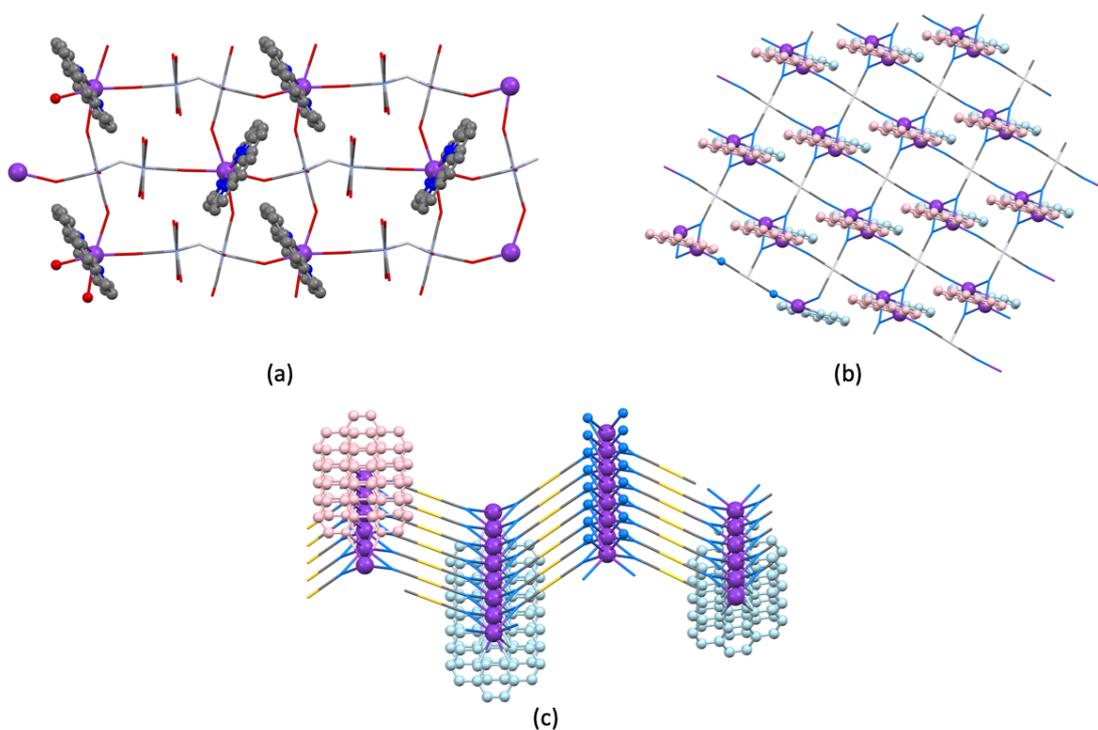
137

138 Figure 3 When 2D structures are formed, the sheets are decorated by oligopyridine ligands above and below the
139 plane as seen in the group 1 metal complexes (a) $\{K(phen)_2[(OC)_5Cr(\mu\text{-}H)Cr(CO)_5]\}_n$ (b) $\{K(phen)(Pt(CN)_4\}_n$
140 (phen ligands above the plane are pink, those below sky blue) (c) $\{K(phen)Au(CN)_2\}_n$ (phen ligands above the
141 plane are pink, those below sky blue; in one row of phen ligands the carbon atoms have been omitted to show
142 the bridging phen ligands more clearly). Hydrogen atoms have been omitted for clarity and structural elements
143 other than the oligopyridine and the metal(s) it is coordinated to are represented as capped sticks. Elements are
144 typically coloured with the standard CPK notation.

145

146   To summarize, the group 1 elements form a diverse array of coordination networks

147 with oligopyridine ligands. Although 1D polymers are common, 2D networks are also

148 known. The bonding between the oligopyridine and the metal ion is primarily ionic and the

149 lack of directionality results in the relatively common observation of bridging oligopyridines

150 in which a single nitrogen atom interacts with two metal centres. We also note that in many

151 cases uncoordinated aza-aromatic ligands are found in the structures of the group 1 metal

152 complexes and X-ray structural determinations are critical to revealing such structural details.

153

Group 2 elements

155 As with the group 1 elements, the chemist does not immediately think of oligopyridine

156 ligands as optimal for group 2 elements. Nevertheless, a rich and interesting coordination

157 chemistry with these ligands exists, and once again many of the complexes considered in this

158 survey are 1D polymers. The compounds $\{Ca(bpy)(\mu\text{-}Br)_2\}_n,$[19] $\{Ba(bpy)(HOMe)_2(\mu\text{-}$

159 $Br)_2\}_n$[20] and $\{Mg(tpy)(OH_2)(\mu\text{-}Pt(CN)_2(\mu\text{-}CN)_2\}_n$ (Fig. 4a, tpy = 2,2':6',2''-terpyridine)[21]

160 are all Type 2 coordination polymers. In contrast to the complexes with group 1 metals, the

161 group 2 metals typically form 1D polymers with two or more oligopyridine ligands per metal

162 centre. As with the 1:1 M:L complexes, a number of structural paradigms may be identified.

163 The simplest can be described as having the oligopyridine ligands arranged *trans* giving the

164 decoration on both sides of the polymer at each metal centre. This pattern is seen in

165 $\{Ba(bpy)_2(\mu\text{-}ClO_4)_2\}$ (Fig. 4b)[19] and $\{Ba(bpy)_2(\mu\text{-}SCN)(\mu\text{-}NCS)\}_n$ [22] A *cis*-arrangement of

166 the oligopyridines at the group 2 metal centre is found in $\{Sr(phen)_2(dmf)_2(\mu\text{-}$

167 $Fe(CN)_3(NO)(\mu\text{-}CN)_2\}_n$ (Fig. 4c),[23,24,25] and the closely related complex

168 $\{Ba(OH_2)_2(phen)_2(\mu\text{-}OH_2)_2Ba(OH_2)_2(phen)_2[\mu\text{-}Fe(CN)_4(\mu\text{-}CN)_2]\cdot Cl\cdot 2phen\cdot 3H_2O\}_n.$[26] The

169 structure of $\{Ba(bpy)_2(\mu\text{-}I)_2\}_n$ shows alternating *up-down* cis-Ba(bpy)$_2$ units reminiscent of

170 the Type 2 chain (Fig. 4d).[19] Another type of 1D polymer is found containing 1:3 group 2

171 metal   to   oligopyridine   ratios,   typified   by   the   compound   reported   as

{Ba(phen)$_3$(OH$_2$)][Fe(CN)$_4$(μ-CN)(μ-NO)}$_n$ (Fig. 4e).[27] The data in the Cambridge Structural Database [4] (Refcode QAGYEE) seem to refer to a compound formulated {[Ba(phen)$_3$(OH$_2$)][μ-Fe(CN)$_4$(μ-CN)(μ-CN)][Ba(phen)$_3$(OH$_2$)](μ-Fe(CN)$_4$(μ-NO)$_2$}$_n$ whereas the original manuscript clearly describes nitroprusside complexes. The final example of a 1D polymer, {Ca$_3$(OH$_2$)$_8$(phen)$_5$[W(CN)$_4$Te$_4$]}$_n$ exhibits a new structural feature of Ca(OH$_2$)$_4$(phen) and Ca(OH$_2$)$_3$(phen)$_2$ "spikes" decorating a 1D polymer chain of the constitution {Ca$_3$(OH$_2$)$_8$(phen)$_5$[W(CN)$_4$Te$_4$]}$_n$ in which the bridging units are W$_4$Te$_4$(CN)$_{12}$ heterocubane clusters (Fig. 4f).[28]

(a) (b) (c) (d) (e) (f)
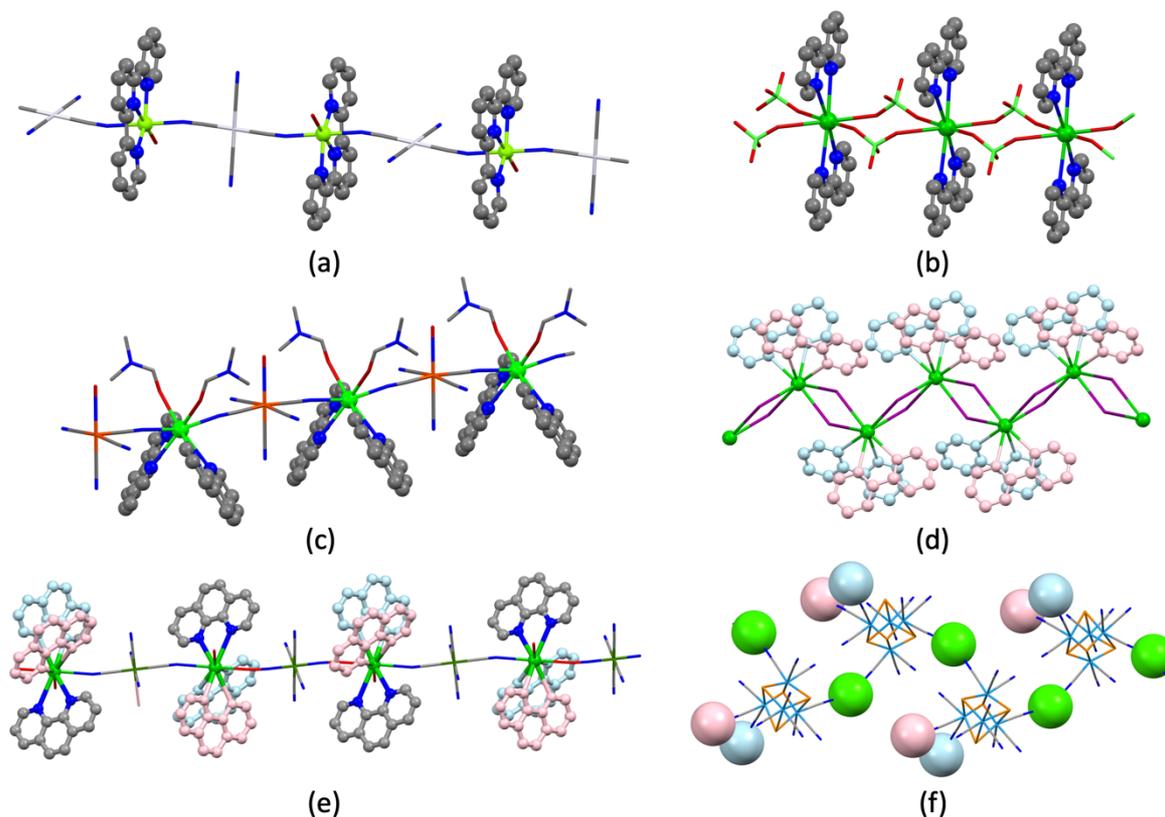
Figure 4 1D polymers are commonly found with group 2 metal centres:(a) {Mg(tpy)(OH$_2$)(μ-Pt(CN)$_2$(μ-CN)$_2$}$_n$ (b) {Ba(bpy)$_2$(μ-ClO$_4$)$_2$}$_n$ (c) {[Ba(OH$_2$)$_2$(phen)$_2$(μ-OH$_2$)$_2$Ba(OH$_2$)$_2$(phen)$_2$(μ-Fe(CN)$_4$(μ-CN)$_2$]Cl·2phen·3H$_2$O}$_n$ (d) {Ba(bpy)$_2$(μ-I)$_2$}$_n$ (*cis*-bpy ligands facing forwards in pink and facing backwards in sky blue) (e) {[Ba(phen)$_3$(OH$_2$)][μ-Fe(CN)$_4$(μ-CN)$_2$][Ba(phen)$_3$(OH$_2$)](μ-Fe(CN)$_4$(μ-NO)(μ-NO)}$_n$ (phen ligands facing forwards in pink and facing backwards in sky blue) and (f) {Ca$_3$(OH$_2$)$_8$(phen)$_5$[W(CN)$_4$Te$_4$]}$_n$ (the Ca(OH$_2$)$_4$(phen) and Ca(OH$_2$)$_3$(phen)$_2$ "spikes" and the bridging Ca(OH$_2$)(phen)$_2$ units are represented as pink, sky blue and green spheres respectively). Hydrogen atoms have been omitted for clarity and structural elements other than the oligopyridine and the metal(s) it is coordinated to are represented as capped sticks. Elements are typically coloured with the standard CPK notation.

191 The transition between 1D and 2D structures is observed in the complex

192 $[Sr(phen)_2(OH_2)_2]_3[Fe(CN)_6]_2$ (Fig. 5a). One μ-$\{Fe(CN)_2(\mu$-$CN)_4\}$ unit bridges to four

193 $Sr(phen)_2(OH_2)$ centres through the equatorial cyanido ligands; two *cis*-$Sr(phen)_2(OH_2)$

194 centres then coordinate to a second μ-$\{Fe(CN)_2(\mu$-$CN)_4\}$ unit. The two remaining

195 $Sr(phen)_2(OH_2)$ each bind a μ-$\{Fe(CN)_4(\mu$-$CN)_2\}$ bridging ligand to give an attractive looped

196 structure with alternating tetranuclear and octanuclear rings (Fig. 5a).[29] The compound

197 $\{Sr(tpy)[Au(CN)_2]_2\}_n$ builds a 2D network decorated top and bottom with the tpy ligands

198 (Fig. 5b); the tpy ligands then form face-to-face π-stacks with the next sheet, each interaction

199 involving two of the three pyridine rings of each ligand (angle between stacked ring planes =

200 2.0$^{\rm o}$, inter-centroid distance = 3.66 Å).[21]

201 The remaining group 2 compounds are all 3D networks with $\{M(tpy)[Pt(CN)_4]\}_n$ (M

202 = Ca, Sr or Ba) forming 3D binodal 4-connecting nets (Fig. 5c) decorated in the voids with

203 the tpy ligands. [21] Finally, we come to $\{Ba(phen)_2(H_2O)_2[Nb_6Cl_{12}(CN)_6]\}_n$ in which each

204 $Nb_6Cl_{12}(CN)_6$ cluster bridges to six $Ba(phen)_2(H_2O)_2$ centres through bridging cyanido

205 ligands; each barium is, in turn, connected to three $Nb_6Cl_{12}(CN)_6$ clusters to give a 3D

206 structure.[30] It is perhaps appropriate to reiterate the comments of Allan White himself, that

207 the "contrariness of Mother Nature" ensures that we cannot understand the idiosyncracies of

208 the group 2-oligopyridine systems.[19]

209

210 Group 13 elements

211 In contrast to the diversity of structures with groups 1 and 2, the majority of the extended

212 structures known containing group 13 metals exhibit 2D structures. Nevertheless, a number

213 of 1D polymers are known with gallium centres. Hydrothermal synthesis has proved popular

214 for the preparation of group 13 oligopyridine complexes and a type 1 structure is exhibited by

215 the compound $\{Ga(phen)(IO_3)_3(\mu$-$IO_3)\}_n$ [31], whereas $\{Ga(bpy)(\mu$-$IO_3)(\mu_2$-$I_2O_7)\cdot HIO_3\}_n$,[31]

216 $\{Ga(phen)(\mu$-$H_2PO_4)(\mu$-$HPO_4)\cdot H_2O\}_n$,[32] $\{Ga(phen)(H_2PO_4)(\mu_3$-$HPO_4)\cdot 1.5H_2O\}_n$[32] and

217 $\{Ga(bpy)(H_2PO_4)(\mu_3$-$HPO_4)\}_n$[33] are all Type 2 with the orientation of the decorating

218 oligopyridines alternating along the polymer chain. The latter two compounds are of interest

219 in possessing a ladder-like core in the direction of propagation of the 1D polymer (Fig. 5d).

(a)

(b)

(c)

(d)
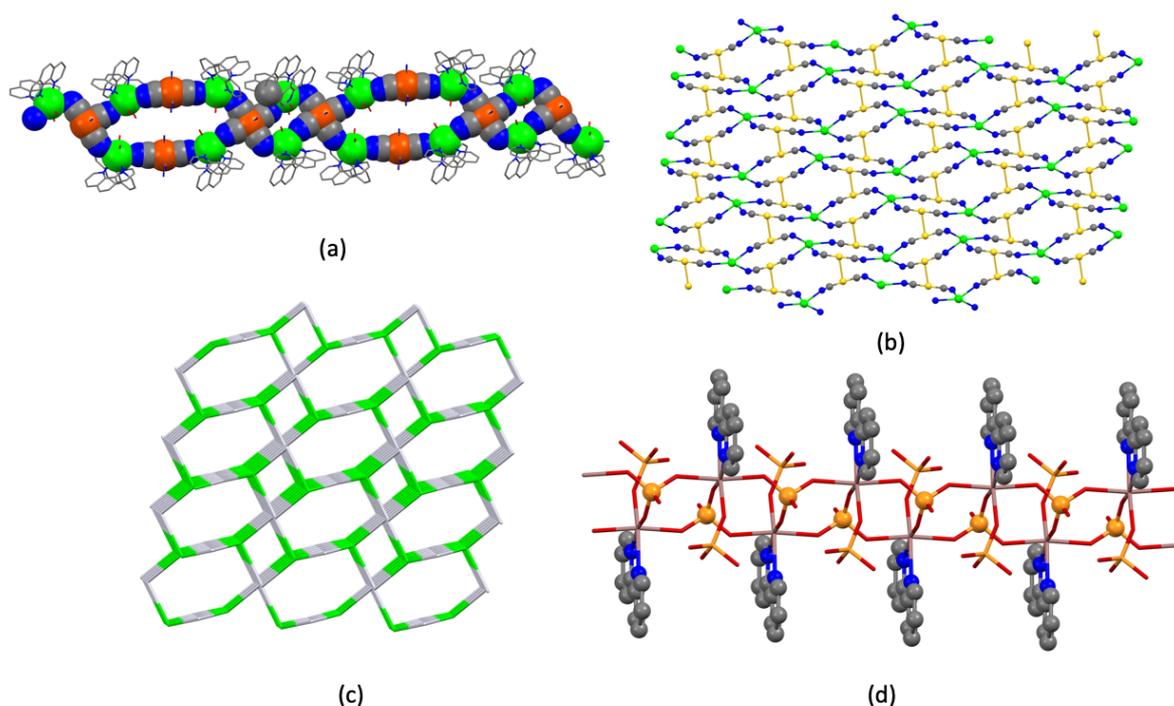
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221   Figure 5 (a) The looped structure observed in $\{[Sr(phen)_2(OH_2)_2]_3[Fe(CN)_6]_2\}_n$. The network connectivity is

222   shown in space-filling representation, other atoms as tubes; (b) the 2D network found in $\{Sr(tpy)[Au(CN)_2]_2\}$

223   showing the Au-Au bonds (Au–Au = 3.1415(4) Å) that link 2D chains together; (c) the binodal 4-connecting

224   nets found in $\{M(tpy)[Pt(CN)_4]\}_n$ (M = Ca, Sr or Ba; (d) part of the Type 2 1D polymer chain in

225    $\{Ga(bpy)(H_2PO_4)(\mu_3\text{-}HPO_4)\}_n$.

226

227   The most common structural motif with group 2 metals appears to be a 2D sheet decorated

228   with oligopyridines top and bottom. This general structure type is found in the compounds

229    $\{Ga(bpy)(\mu\text{-}HPO_4)(\mu\text{-}H_2PO_4)\}_n,$[34] $\{Al(bpy)(\mu\text{-}HPO_4)(\mu\text{-}H_2PO_4)\}_n,$[35] $\{Ga_2(phen)(\mu_3\text{-}$

230    $HPO_4)_2(\mu\text{-}HPO_4)\}_n$ (Fig.   6a)   [36] $\{In_4(bpy)_2(H_2O)_2(\mu\text{-}OH)(\mu_3\text{-}SO_4)_2(\mu\text{-}SO_4)_2\}_n,$[37]

231    $\{Ga_2(bpy)F(H_2O)(\mu_3\text{-}HPO_4)_2(\mu\text{-}F)\}_n,$[38] $\{Ga_2(phen)F(H_2O)(\mu_3\text{-}HPO_4)_2(\mu\text{-}F)\}_n,$[39]

232    $\{In_2(bpy)F(H_2O)(\mu_3\text{-}HPO_4)_2(\mu\text{-}F)\}_n,$ [40] $\{In_2(3\text{-}H_2Nbpy)F(H_2O)(\mu_3\text{-}HPO_4)_2(\mu\text{-}F)\}_n,$[40]

233    $\{Ga_3(bpy)_2(\mu_3\text{-}PO_3)_2(\mu\text{-}PO_3)(\mu\text{-}HPO_3)(\mu\text{-}F)_2\}_n,$[41] all of which are prepared by hydrothermal

234   methods. Two very different structures are found for the compounds $\{In_2(phen)(H_2O)(\mu\text{-}$

235    $IO_3)_3(IO_3)_3 \cdot H_2O\}_n$ (Fig. 6b) and $\{In_2(bpy)(H_2O)(\mu\text{-}IO_3)_3(IO_3)_3 \cdot H_2O\}_n$ in which the 2D sheets

236   are only decorated with the phen ligands on one face.[31]   A hierarchical structure then

237   develops in which face-to-face interactions of the undecorated faces, with additional In...O

238   interactions, build a double layer, which in turn, through face-to-face π-stacking of the

239   oligopyridine ligands extends to give a supramolecular 3D structure.

9

(a)

(b)
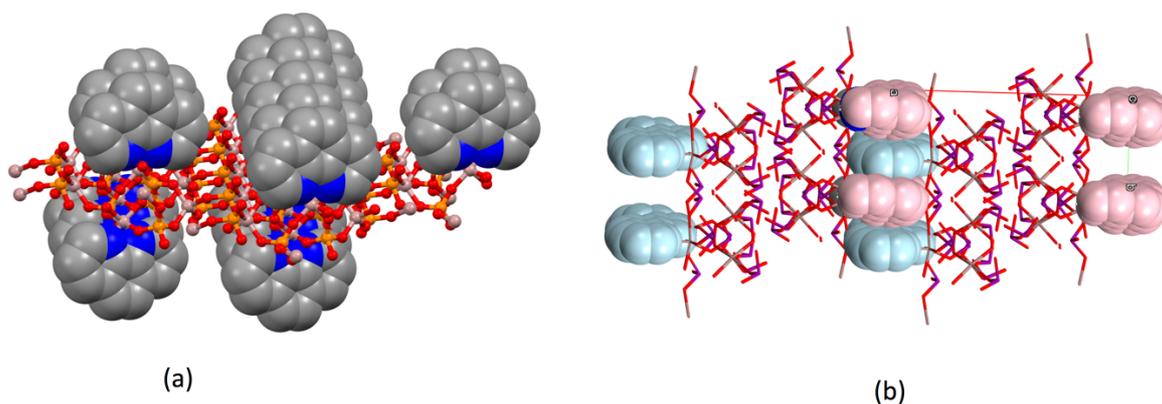
Figure 6 (a) The typical arrangement of oligopyridine ligands above and below a 2D sheet constructed from group 2 metals and bridging anions, in this case showing $\{Ga_2(phen)(\mu_3\text{-}HPO_4)_2(\mu\text{-}HPO_4)\}_n$ and (b) the decoration of a 2D sheet on only one face leads to the development of a supramolecular 3D structure as seen in $\{In_2(phen)(H_2O)(\mu\text{-}IO_3)_3(IO_3)_3\cdot H_2O\}_n$; the oligopyridine ligands have been coloured sky blue and pink to emphasize the π-stacking.

Group 14 elements

The vast majority of relevant oligopyridine complexes of group 14 elements involve lead, although $\{Sn(phen)Cl_2\}_n$ is of some interest. The compound $[Sn(phen)Cl_2]$ was originally described as exhibiting unusual additional Cl…Sn interactions > 2.8 Å and with Sn…Sn distances of 4.290 and 4.701 Å giving a loosely connected polymeric structure.[42] Very recently a polymorph has been reported which is formulated as a 1D-coordination polymer with Cl–Sn distances of 2.732 and 2.549 Å, Sn…Sn 3.897 Å and comprising an $\{Sn(\mu\text{-}Cl)_2\}_n$ chain decorated with phen ligands on each tin in a 1D-alternate arrangement (Fig. 7a). [43]

(a)

(b)

(c)

(d)
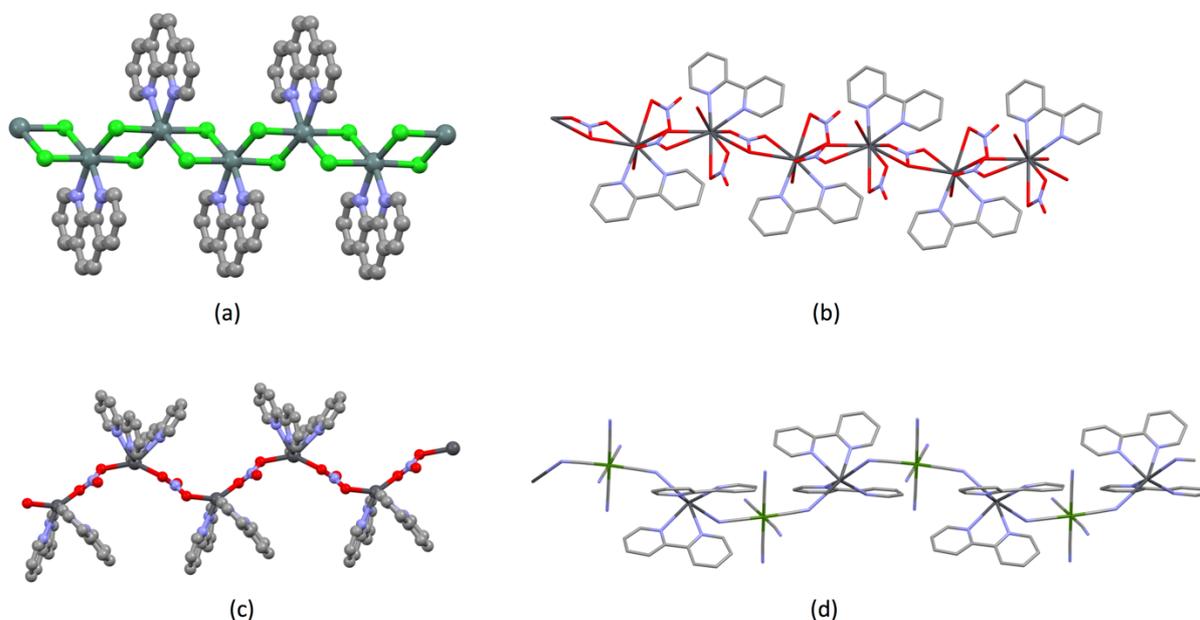
Figure 7 1D coordination polymers incorporating group 14 metal centres (a) $\{Sn(phen)Cl_2\}_n$ (b) $\{Pb(bpy)(NO_3)(OH_2)(\mu\text{-}NO_3)\}_n$ (c) $\{[Pb(bpy)_2(\mu\text{-}NO_3)](PF_6)\}_n$ (d) the $\{Pb(bpy)_2(\mu\text{-}Fe(CN)_6)\}$ chain found in $\{[Pb(bpy)_2]_6[Fe(CN)_6]_4\cdot bpy\cdot14H_2O\}_n$.

260 As mentioned above, the vast majority of compounds with group 14 metals involve lead, and

261 the number of structurally characterized compounds appears to be anomalously high. This

262 may be associated with the interest in assigning structural effects to a "stereochemically

263 active lone pair". Numerous compounds of the type $\{PbL(\mu-X)_2\}_n$, $\{PbL(\mu-X)(\mu-Y)\}_n$,

264 $\{Pb_2L_2(\mu-X)_3(\mu-Y)\}_n$ and $\{PbL((\mu-X)Y\}_n$ (L = bpy, 4'-Cltpy, 4,5-diazafluoren-9-one, 5-

265 H_2Nphen, 2,9-Me$_2$phen, 4,4'-MeO$_2$bpy, phen, tpy; X, Y = Br, Cl, ClO$_4$, [Hg(CN)$_2$(μ-Cl)$_2$],

266 [μ-Pt(SCN)$_4$], I, N$_3$, NO$_3$, SCN) are known and form Type 2 polymers decorated with an

267 oligopyridine on each lead atom.[44–72] A closely related motif is found in polymorphs of

268 $\{Pb(bpy)(NO_3)(OH_2)(\mu-NO_3)\}_n$ (Fig. 7b) and $\{Pb(phen)(NO_3)(OH_2)(\mu-NO_3)\}_n$ in which the

269 alternating oligopyridine ligands are somewhat flattened.[73–78] More complex Type 2

270 structures are found in $\{Pb(bpy)(\mu_3-SCN)_2\}$ in which each thiocyanato ligand bridges three

271 metals in a $\kappa 1S:\kappa 2S:\kappa 3N$ manner,[60,67,79] and in $\{Pb(4,4'-Me_2bpy)(\mu_3-SCN)(\mu-SCN)\}_n$,[80]

272 $\{Pb(phen)(NO_3)(\mu_3-NCNCN)\}_n$,[81] $\{Pb(bpy)(H_2O)(\mu_3-NCNCN)(NCNCN)\}_n$,[81] $\{Pb(4,4'-$

273 (MeO)$_2$bpy)(μ-NCNCN)(μ-NO$_3$)$\}_n$[82] and $\{Pb(tpy)(\mu_4-NCNCN)(\mu_2-NCNCN)\cdot H_2O\}_n$[83] in

274 which multiple cyanamide bonding modes are exhibited.

275

276 A rather special 1D polymer is found in $\{Pb(bpy)(B_6H_6)\}_n$ in which each *closo*-

277 $[B_6H_6]^{2-}$coordinates to three lead centres through a triangular face giving overall a Type 2

278 structure.[84] The coordination of an additional oligopyridine ligand to each metal of the Type

279 2 coordination polymer gives compounds such as $\{[Pb(bpy)_2](\mu-NO_3)](PF_6)\}_n$ (Fig. 7c),[85]

280 $\{Pb(bpy)_2)(\mu-[Au(CN)_2]_2\}_n$[86] and $\{[Pb(bpy)_2][\mu-Pt(SCN)_4]\}_n$.[87] Similarly, the 1D

281 $\{Pb(bpy)_2(\mu-Fe(CN)_6)\}$ chain found in $\{[Pb(bpy)_2]_6[Fe(CN)_6]_4\cdot bpy\cdot 14H_2O\}_n$ corresponds to

282 the addition of an additional bpy ligand to each lead centre in a flattened alternating 1D

283 structure (Fig. 7d).[88] The linking together of two 1D chains by bridging ligands gives

284 ladder-like structures and very nice examples are seen in $\{(\{Pb(4'-Brtpy)[\mu-Au(CN)_2]\}_2(\mu-$

285 OH$_2$))[Au(CN)$_2$]$_2$·0.48H$_2$O$\}_n$ in which the rails of the ladder are $\{Pb(4'-Brtpy)[\mu-Au(CN)_2]\}$

286 chains and the bridging water molecules form the rungs (Fig. 8a) and in $\{\{Pb(4'-Cltpy)[\mu-$

287 Au(CN)$_2$]$\}_2$[μ-Au(CN)$_2$]$_2\}_n$ in which the rungs are formed by the bridging [μ-Au(CN)$_2$]$_2$

288 units. [89]

289 The reaction of PbCl$_2$ with 2,9-Me$_2$phen in MeOH gives the 1D polymer $\{Pb_3(2,9-$

290 Me$_2$phen)$_2$(μ_3-Cl)$_2$(μ-Cl)$_4\}_n$ which has a Pb$_3$Cl$_6$ core decorated on two of the three lead

291 centres with the oligopyridine (Fig. 8b).[90] The structure of the 1D polymers with $\{Pb_3(4'-$

pytpy)$_2$(μ_3-Cl)$_2$(μ-Cl)$_4$·MeOH}$_n$[91] and {Pb$_3$(4,4'-(MeO)$_2$bpy)$_2$(μ-Br)$_6$}$_n$ [46] are somewhat similar, with the two external lead centres being decorated with the 4'-pytpy ligands (4'-pytpy = 4'-(4-pyridyl)-2,2':6',2"-terpyridine). This compound has been used as a precursor for the preparation of PbO nanoparticles.[92] The thermal decomposition of the 1D polymeric complex {Pb$_3$(3,4,7,8-Me$_4$phen)$_4$(μ-N$_3$)$_5$(μ-NO$_3$)}$_n$ also leads to PbO nanoparticles.[93] The polynuclear motif is also extended into decorated 2D sheets. One particularly interesting example is the compound {[Pb$_2$(phen)(μ_3-N$_3$)(μ-N$_3$)$_2$](ClO$_4$)}$_n$ in which the lead azido central 1D cylinder is decorated with four bpy ligands (Fig. 8c).[94]

The remaining lead-containing structures are 2D sheet structures of various types, decorated top and bottom with the oligopyridine ligands. In {Pb(tpy)[μ-M(CN)$_2$]$_2$}$_n$ (M = Ag or Au), the dicyanidometallate ligands bridge top and bottom surfaces of lead centres, each of which bears a tpy capping ligand,[95] and a similar structure is found in {Pb(4'-HOtpy)[μ-Au(CN)$_2$]$_2$}$_n$.[83] Broadly similar is the 2D sheet in {[Pb(bpy)$_2$[μ-Pt(SCN)$_4$]}$_n$ in which the [μ-Pt(SCN)$_4$] ligands bridge upper and lower lead centres each bearing two bpy ligands.[72] In contrast to these structures, which can be described as a double sheet structure with two different lead-containing layers top and bottom with one oligopyridine on each lead, the sheet in {[Pb(bpy)$_2$[μ-Au(CN)$_2$]$_2$}$_n$ is only "one lead thick" and each lead bears two bpy ligands, one top and one bottom.[86] The compound {[Pb(bpy)[Ag$_3$(μ_4-I)(μ_3-I)(μ-I)$_3$]}$_n$ is best described as an Ag$_3$I$_5$ sheet decorated top and bottom with Pb(bpy) motifs.[96]

(a)

(b)

(c)

Group 15 elements

Three polymeric compounds have been reported with group 15 elements coordinated to an oligopyridine and all are 1D-polymers. The simplest is {Bi$_2$(phen)$_2$Br$_5$(NO$_3$)}$_n$, which is obtained from the reaction of Bi(NO$_3$)$_3$ with KBr and phen, and consists of a 1-D chain in which each bismuth is decorated with a phen to give a distorted structure close to the Type 2 arrangement (Fig. 9a).[97] Similarly, the reaction of Bi(NO$_3$)$_3$ with Ag(NO$_3$), NaI and phen gave {Bi(phen)I$_4$Ag(phen)}$_n$ containing a 1D chain with each Ag and Bi decorated with a phen in a 1D-alternate arrangement (Fig. 9b). [96] The final example is also polymetallic and formally described as the salt [As(phen)]$_2$[As$_2$Mo$_2$O$_{14}$]; the best description is as a 1D-As$_4$Mo$_2$O$_{14}$ polymer in which the peripheral arsenic atoms are decorated with phen ligands (Fig. 9c).[98]

(a)　　　　　　　　　　　　(b)

(c)
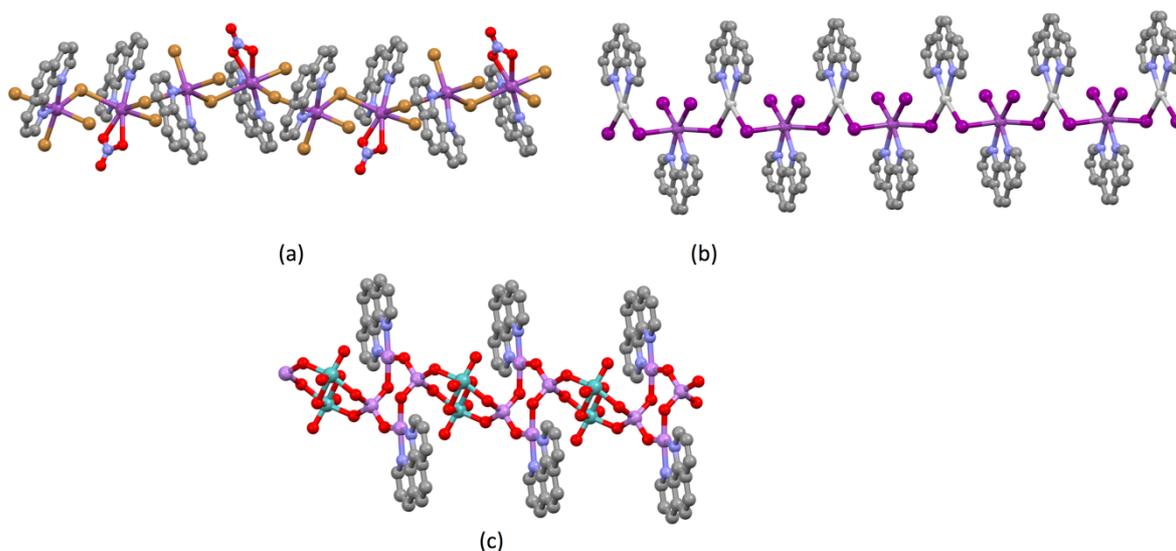
Figure 9. (a) Parts of the polymeric structures of {Bi$_2$(phen)$_2$Br$_5$(NO$_3$)}$_n$, (b) {Bi(phen)I$_4$Ag(phen)}$_n$ (c) {[As(phen)]$_2$[As$_2$Mo$_2$O$_{14}$]}$_n$

Conclusions

A survey of structurally characterized oligopyridine complexes of the main-group metals from groups 1, 2, 13, 14 and 15 illustrates a diverse array of 1D chains (including ladder assemblies) and 2D networks. In most assemblies, the polymeric array is defined by the metal atoms and bridging ligands other than oligopyridines; the latter feature as peripheral

decorations, often engaging in face-to-face π-stacking interactions. In 1D coordination

polymers, three types of decoration predominate which we have defined at Type 1 (all the

oligopyridines on the same side and π-stacked, Type 2 (alternating arrangement of

oligopyridines) abd Type 3 (a pairwise alternating structure).

Conflicts of interest

The authors declare no conflicts of interest

Acknowledgements

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