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Review

Expanded ligands—An assembly principle for supramolecular chemistry

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Contents

Abstract

Expanded ligands incorporate metal-containing groups as spacers between metal-binding domains. This article presents the principle and analyses expanded ligands based upon $\{M(tpy)_2\}$ (tpy = 2,2′:6′,2″-terpyridine) scaffolds.

Keywords: Supramolecular; 2,2′:6′,2″-terpyridine; Crystal engineering; Coordination chemistry

1. Introduction

We recently introduced the term “expanded ligands” to describe ditopic species in which the metal-binding domains are separated by a metal-containing unit [1–8]. In this article, we further explore the utility of this concept in supramolecular and metallosupramolecular chemistry and in crystal engineering. We believe that expanded ligands could become an important and useful design principle in these and related areas. In particular, the expanded ligand approach allows the facile introduction of metal-centred properties such as redox- or photoactivity. The article commences with a definition of an expanded ligand and then explores the utility of the concept in supramolecular and structural chemistry.

2. The expanded ligand concept

Multitopic ligands with two or more discrete metal-binding domains separated by spacers are key building blocks in synthetic chemistry and materials science. Such ligands are the basis for the preparation of multinuclear complexes and coordination arrays of various dimensionality. Conventional ligands are

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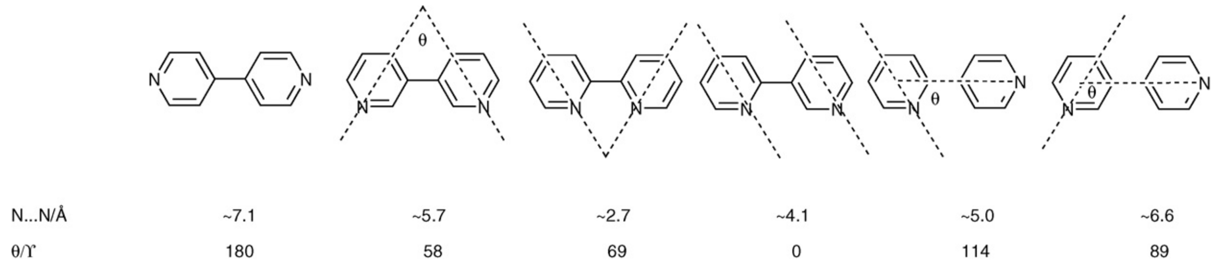


Fig. 1. Systematic variation in donor distance and the vector defining the nitrogen lone pairs in the series of isomeric bipyridines.

usually organic compounds containing donor atoms or groups of donor atoms defining the metal-binding domains and enormous effort has been expended in the design and synthesis of such systems, in particular with respect to the spacers, with a view to optimizing their spatial, electronic and photophysical properties. We have long been interested in the use of metal centres in supramolecular chemistry both as an assembly principle and for the introduction of specific properties and I introduced the term metallosupramolecular chemistry to collectively describe these areas [9], although the necessary metal-ion recognition features had been implicitly or explicitly stated in earlier work [10,11]. In summary, metallosupramolecular chemistry is concerned with the matching up of the characteristic and preferred coordination numbers and coordination geometries of metal ions with the number, type and spatial arrangement of ligand donor atoms. In retrospect, it is apparent that metallosupramolecular chemistry has played a vital role in the development of supramolecular chemistry and that it provided the touchstone for the establishment of many critical concepts. In the refinement of the metallosupramolecular chemistry precepts, a key step was the differentiation between labile and kinetically inert metal centres; specifically, the recognition that labile centres could be used for self-assembly processes leading to thermodynamic products whereas inert centres could be carried through a synthesis as pseudo-organic species. More recently, we recognized that the same concepts may be applied more widely to multifunctional species and offered alternative strategies for the preparation of novel multidentate and multitopic ligands.

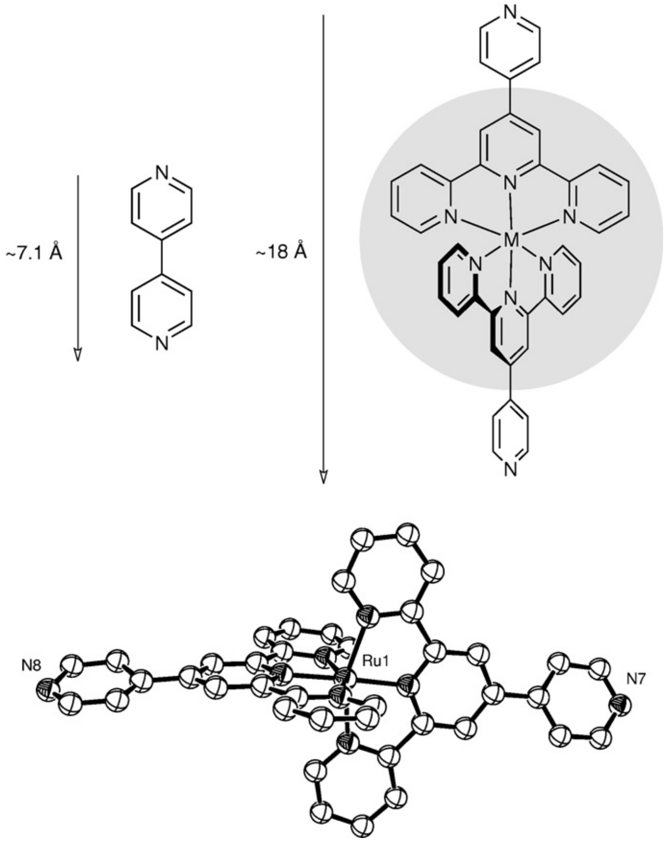
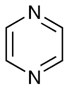


Fig. 2. The expanded ligand concept exemplified in the comparison of 4,4′-bipyridine and a $\{M(\mathbf{7})_2\}^{n+}$ complex and the solid state structure of the $[Ru(\mathbf{7})_2]^{2+}$ cation [7]. The figure illustrates the conceptual partitioning of the expanded ligand into a central metal-containing scaffold, indicated in grey, and pendant metal-binding sites that parallel the parent ligand.



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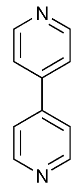

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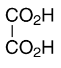

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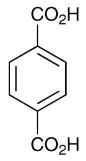

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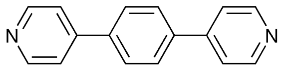

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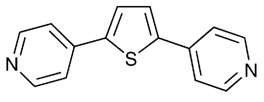

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It has long been recognized that ligands such as pyrazine **1** and 4,4′-bipyridine **2** or oxalic acid **3** and terephthalic acid **4** are topologically and conceptually related. Specifically, 4,4′-bipyridine can be regarded as an expanded pyrazine in which the N· · ·N distance has increased from ∼2.8 Å [12–14] to ∼7.1 Å [15–17] and terephthalic acid as an analogue of oxalic acid in which the carboxylic acid carbon C· · ·C distance has increased from ∼1.5 Å [18–21] to ∼5.7 Å [22–25]. In these cases, the expansion of the ligand is through covalent “organic” chemistry and the use of conventional spacers. Naturally, by selecting isomeric compounds, both the distances and the vectorial relationships of the donors may be varied in a well-defined manner. This is illustrated in Fig. 1 for the isomeric bipyridines in which the nitrogen atoms are variously chelating or divergent, the latter arrangement giving rise to a bridging ligand. The angles θ refer to the planar conformations depicted and rotation about the interannular bond will generate a range of such angles. All of the bipyridines, including 2,2′-bipyridine in its trans conformation, can act as bridging ligands but only 2,2′-bipyridine can act as a chelating ligand.

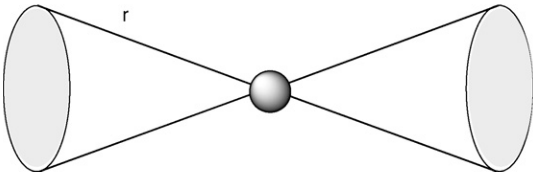
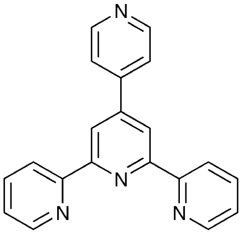


Fig. 3. Expanded ligands in which the donor atoms do not lie along the principal axis are best described in terms of two coaxial cones in which the donors lie in the plane described by the donor atoms through rotation about the principal axis.



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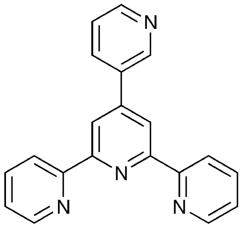

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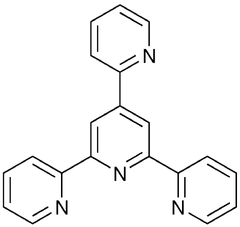

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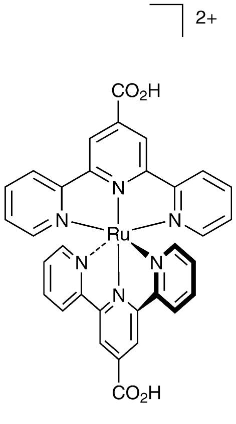
More systematic variation is possible through additional synthesis and ligands such as **5** and **6** illustrate the subtle control over the distance and vectorial properties of the donors that is possible through ligand design. Both **5** and **6** are 4,4′-bipyridine analogues in which the two 4-pyridyl metal-binding domains are separated by an additional aryl group. However, the consequence is a different vectorial relationship between the two nitrogen lone pairs and a different N· · ·N distance. These compounds provide the link between the typical organic ligands and the expanded ligand concept.

Conceptually, in an expanded ligand the spacer groups introduced in **5** and **6** (1,4-phenylene and 2,5-thienylene, respectively) are replaced by metal-containing moieties. A prototypical example is seen in the comparison of 4,4′-bipyridine with $\{M(\mathbf{7})_2\}^{n+}$ cations. The linear connectivity across the 4′-substituted 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine ligands makes the analogy particularly clear and the N· · ·N distance increases from ∼7.1 Å in 4,4′-bipyridine to ∼18 Å in a series of $\{M(\mathbf{7})_2\}^{n+}$ complexes with various charges and metal centres (Fig. 2) [6,7,26–28]. We have discussed elsewhere the influence of crystal packing effects on the precise conformation of the $\{M(\mathbf{7})_2\}^{n+}$ cations and note that distortion of the cation leads to small and unpredictable variations in the N· · ·N distances. We had hoped that a more rational control over distance would be obtained on varying the size of the metal ion but on moving from $[\mathrm{Fe}(\mathbf{7})_2]^{2+}$ [26] to $[\mathrm{Ru}(\mathbf{7})_2]^{2+}$ [7] the N· · ·N distance only increases negligibly.

Expanded ligand analogues of the various bipyridine isomers can be formed by using the isomeric tpy ligands with pendant 3-pyridyl (**8**) or 2-pyridyl (**9**) groups. The solid state structures of $[M(\mathbf{8})_2]^{n+}$ [29–31] and $[M(\mathbf{9})_2]^{n+}$ [29] cations confirm that there are changes in the N· · ·N distances. The precise N· · ·N distances and vectorial relationship of the nitrogen lone pairs depends upon the interannular angles between the pendant 4-pyridyl ring and the central tpy ring to which it is attached. This problem is illustrated in the N· · ·N distances in structurally characterized $[\mathrm{Ru}(\mathbf{8})_2]^{2+}$ and $[\mathrm{Ru}(\mathbf{9})_2]^{2+}$ salts of ∼16.8 Å and ∼13.5 Å, respectively. The most useful way of considering these compounds in which the donor atom does not lie along the principal axis, is to consider two coaxial cones with their vertices at the metal centre and the base being the plane in which the donor atoms lie (Fig. 3). In the case of $[\mathrm{Ru}(\mathbf{9})_2]^{2+}$ r (the Ru· · ·N distance) is ∼6.8 Å and, as expected, it is greater in $[\mathrm{Ru}(\mathbf{8})_2]^{2+}$ where r is ∼8.4 Å.

Continuing with the $\{\mathrm{Ru(tpy)_2}\}$ core as the metal-containing moiety, we see that the carboxylic acid complexes **10** and **11** could be viewed as expanded oxalic or terephthalic acids [8]. The carboxylic acid C· · ·C distances in complexes **10** and **11** are increased to ∼12.5 Å and ∼21 Å, respectively.



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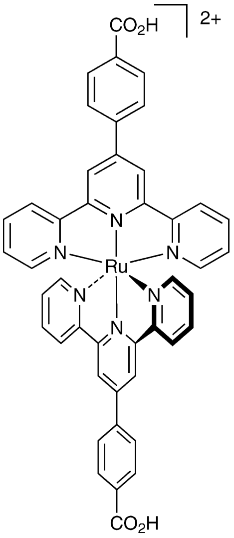

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To summarize, *expanded ligands* are analogues of conventional ligands in which the donor sites are separated by metal-containing groups. It is convenient to partition the expanded ligands into a central metal-containing scaffold and pendant metal-binding sites that parallel the parent ligand. There is an obvious analogy to the “complexes as metals, complexes as ligands” strategy developed for the synthesis

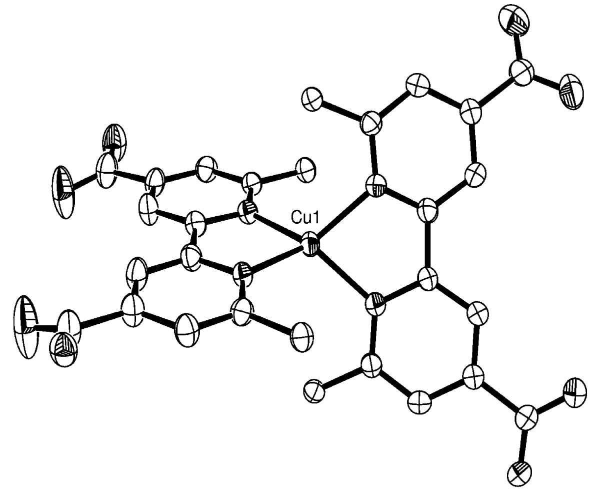
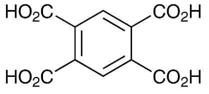


Fig. 4. Ligands bearing two carboxylic acid substituents can form 1:2 complexes which may be regarded as expanded pyromellitic acids. The crystal structure of the cation present in $[\mathrm{CuL_2}][\mathrm{PF_6}]$ (L = 6,6′-diphenyl-2,2′-bipyridine-4,4′-dicarboxylic acid, **15**) with only the *ipso* carbon atoms of the phenyl groups shown [36].

of metallodendrimers [32–35], but represents a broader perspective. In particular, the novel aspect is the potential for self-assembly of the expanded ligand using labile metal centres, obviating the need for covalent synthesis of spaced systems and the opportunity for in-built error correction. Although this article will concentrate upon the use of oligopyridine ligands such as 2,2′-bipyridine (bpy), 2,2′:6′,2″-terpyridine (tpy) and 1,10-phenanthroline (phen), the concept is more generally applicable to scaffolds incorporating any metal-binding domain.

3. From expanded ligands to topological diversity

One of the advantages of this approach using expanded ligands as building blocks is the ease with which a high degree of molecular and topological diversity can be attained without a significant investment in ligand synthesis. As an example, consider expanded ligand analogues of the tetracarboxylic acid, pyromellitic acid **12**. Using the expanded ligand concept, the complex motif $\{\mathrm{M}(\mathbf{13})_2\}$ becomes an analogue of **12**. However, the recognition that the relationship relies upon a topological identity also leads to other $\mathrm{ML_2}$ complexes $\{\mathrm{M}(\mathbf{14})_2\}$ such as tetrahedral $[\mathrm{Cu}(\mathbf{14})_2]^+$ and square-planar $[\mathrm{Pt}(\mathbf{14})_2]^{2+}$ being identified as analogues of **12**. In the case of $[\mathrm{Cu}(\mathbf{14})_2]^+$ the four carboxylic acid groups would be directed to the vertices of a tetrahedron whereas in $[\mathrm{Pt}(\mathbf{14})_2]^{2+}$ they lie at the corners of a square. It is also obvious that complexes containing $\{\mathrm{M}(\mathbf{15})_2\}$ motifs are analogues of mellitic acid **16** although the carboxylic acids lie on the vertices of an octahedron rather than of a hexagon (Fig. 4).



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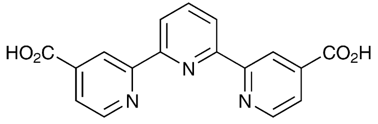

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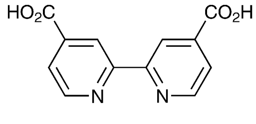

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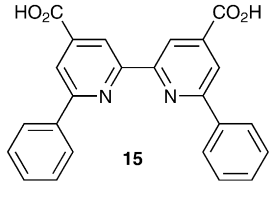

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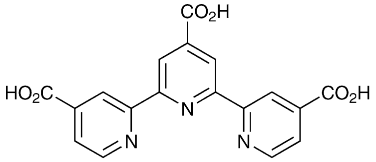

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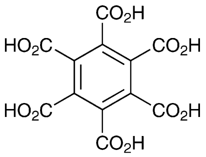

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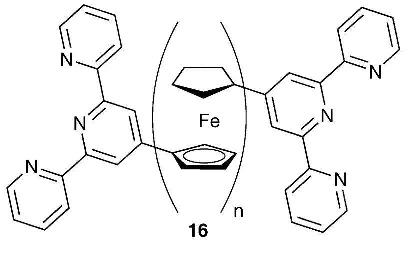
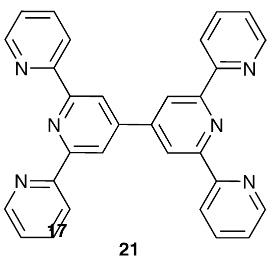
The beauty of the concept becomes clearer when we consider the consequences of a change of scaffold from $\{\mathrm{M(tpy)_2}\}$ to $\{\mathrm{M(bpy)_3}\}$. As noted above, ligand **14**, gives $\{\mathrm{M}(\mathbf{14})_2\}$ complexes which are analogues of pyromellitic acid (**17**) but can also form octahedral $\{\mathrm{M}(\mathbf{14})_3\}$ species which are to be regarded as expanded mellitic acids. We thus have two complementary routes to expanded ligand analogues of mellitic acid utilising different scaffolds. Here we clearly see the advantage of the metal-centred approach over the use of covalently bonded spacers. However, even with six-coordinate metal centres is it possible to build pyromellitic acid analogues in complexes of the type $\{\mathrm{M}(\mathbf{14})_2\mathrm{X}_2\}$. This identity has been explored for the 4,4′-dicarboxylic acid **14** [36–41] and the 5,5′-analogue **21** [37,42]. The replacement of the $\{\mathrm{M(tpy)_2}\}$ scaffold by $\{\mathrm{M(bpy)_3}\}$ or $\{\mathrm{M(bpy)_2X_2}\}$ centres also has the effect of introducing a new stereogenic centre. This has significant consequences for the arrangement of multiple $\{\mathrm{M(bpy)_3}\}$ motifs in supramolecular systems or in extended lattices.

As stated above, this article concentrates upon $\{\mathrm{M(tpy)}_n\}$ and $\{\mathrm{M(bpy)}_n\}$ scaffolds, but the concept is generally applicable to any desired metal-containing scaffold. For example, in an inversion of the usual $\{\mathrm{M(tpy)_2}\}$ motif, compounds **18**–**20** can be regarded as an expanded version of the bis(tpy) **21** in which a 1,1′-ferrocenyl scaffold has been introduced between the metal-binding domains [43–46].

18 n=1
19 n=2
20 n=3





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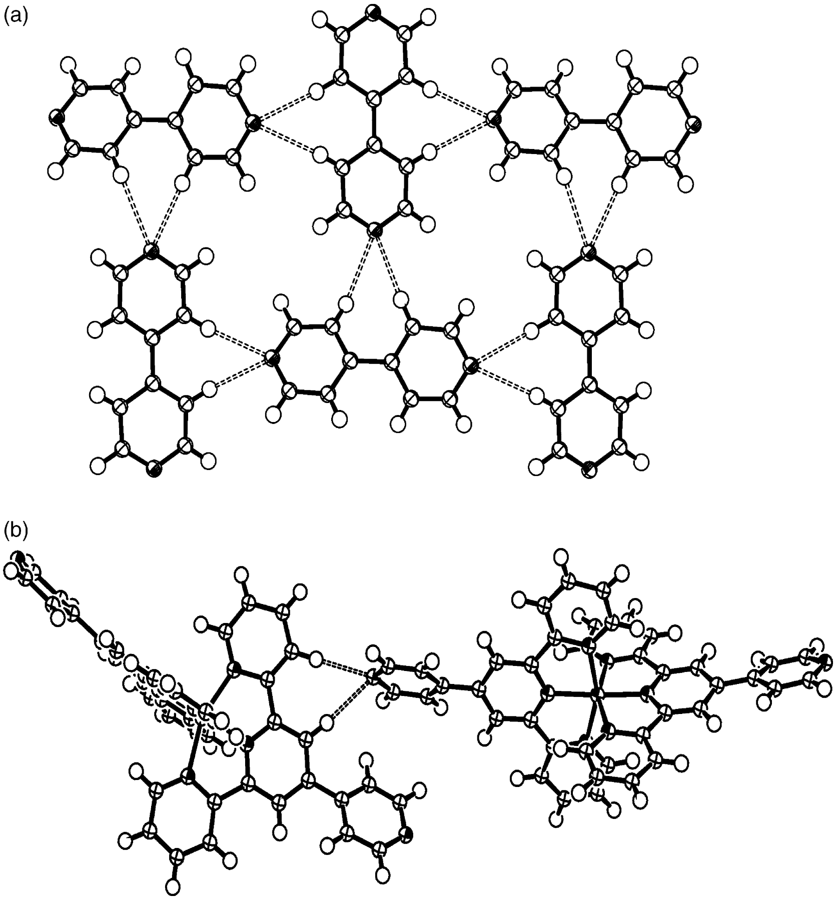


Fig. 5. Solid state structures of (a) 4,4′-bipyridine [15–17] and (b) $[Ru(\mathbf{7})_2][PF_6]NO_3\cdot$dmso [7] illustrating similar N· · ·H–C interactions.

In the preceding sections we have established the formalism of the expanded ligand concept, with a particular emphasis upon $\{M(tpy)_n\}$ or $\{M(bpy)_n\}$ scaffolds. In the following section we will probe the extent of validity of the concept and show that the expanded ligands (i) can possess similar structural features as the parent ligands, (ii) can behave as ligands in a manner analogous to the parent structure forming molecular and supramolecular species and (iii) can form extended one-, two- and three-dimensional structures related to those obtained with the parent ligands.

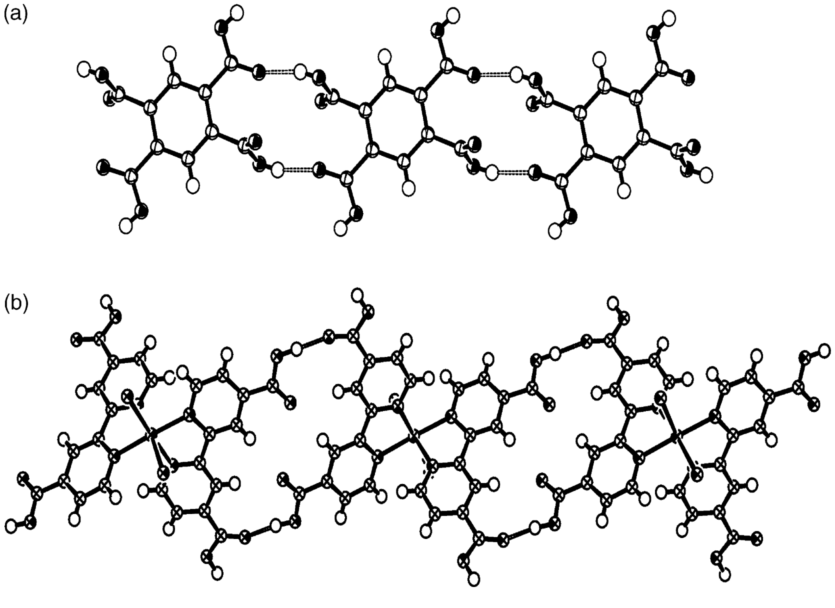
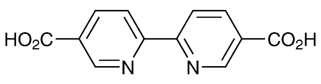


Fig. 6. Solid state structures of pyromellitic acid [47,48] and (b) $[Ru(\mathbf{14})_2Br_2]\cdot H_2O$ [39] illustrating that the O· · ·H–O interactions lead to similar ribbon motifs.

4. Structural analogies between expanded ligands and the parent structures

We start with a comparison of $\{M(\mathbf{7})_2\}$ complexes with 4,4′-bipyridine. Three solid state structural determinations of the free ligand 4,4′-bipyridine [15–17] have been reported and four $\{M(\mathbf{7})_2\}$ complexes have been structurally characterized [2,7,26–28]. As discussed later, we should eliminate one compound [28] from the list. Is it reasonable to expect to find common structural motifs, as opposed to merely topological equivalence, in view of the presence of counterions and significantly different topographies in the expanded ligands? In the solid state, 4,4′-bipyridine forms sheets with weak N···H–C hydrogen bonds (2.632, 2.742 Å) (Fig. 5a). The dominant lattice interactions in the expanded ligands are between cations and anions, with intercation stacking of the pendant 4-pyridyl rings in some cases [7,27], but in the case of $[Ru(\mathbf{7})_2][PF_6]NO_3\cdot dmso$ [7] there is also a motif reminiscent of that in 4,4′-bipyridine with weak hydrogen bonds between the pendant pyridine nitrogen and tpy C–H bonds (2.519, 2.394 Å) (Fig. 5b). Considering that the intermolecular interactions in the lattice of 4,4′-bipyridine are energetically much smaller than those in the expanded ligands, it is remarkable that even this small degree of similarity exists.

Hydrogen bonding between carboxylic acid groups is a much stronger bonding motif than the weak C–H···N interactions in the expanded 4,4′-bipyridine analogues and it might be expected that a closer structural analogy will exist between carboxylic acids and their expanded analogues. Fig. 6a shows part of the hydrogen-bonding network in pyromellitic acid dihydrate [47,48] in which only the direct interactions between carboxylic acid groups are shown. The core motif is a ribbon in which pairs of *ortho*-carboxylic acid groups are hydrogen bonded (O···O, 2.688 Å, ∠O–H···O, 172°) as shown in Fig. 6a. We noted earlier that complexes of the type $\{M(\mathbf{14})_2X_2\}$ are expanded ligand analogues of pyromellitic acid and now analyse the structure of $[Ru(\mathbf{14})_2Br_2]\cdot H_2O$ [39]. Once again, additional hydrogen-bonding interactions (involving the lattice water molecule and the bromide ligands) are ignored and we concentrate upon interactions involving the carboxylic acids. Remarkably, the same ribbon motif is observed (O···O, 2.649 Å, ∠O–H···O, 158°, Fig. 6b) in the complex as in the pyromellitic acid and the structural analogy can be said to be strictly fulfilled.



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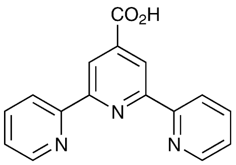
The solid state structures of rhodium(III) and cobalt(III) complexes of 2,2′-bipyridine-5,5′-dicarboxylic acid **22** have been reported by Williams and co-workers [37] and, although they do not closely parallel the structure of mellitic acid, they illustrate a number of general points that serve to potentially limit structural analogies. Firstly, the charge on the metal complex reduces the pK_a of the carboxylic acid and it is difficult to control the formation of Zwitterionic species in which one or more carboxylic acids are deprotonated. Naturally, the carboxylate–carboxylic acid interactions will differ in kind and magnitude from carboxylic acid–carboxylic acid interactions and in the case of fully deprotonated species carboxylate–carboxylate interactions are expected to be repulsive. Secondly, the expansion of the ligand could result in large crystal voids, and the tendency to form interpenetrated structures is increased [49]. Whilst this may not alter the topology of the sub-networks it will increase the complexity of the packing significantly.



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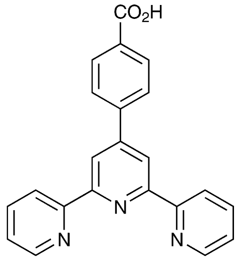

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These influences, together with the tendency for ionic lattices to incorporate solvent are also the dominant factors in

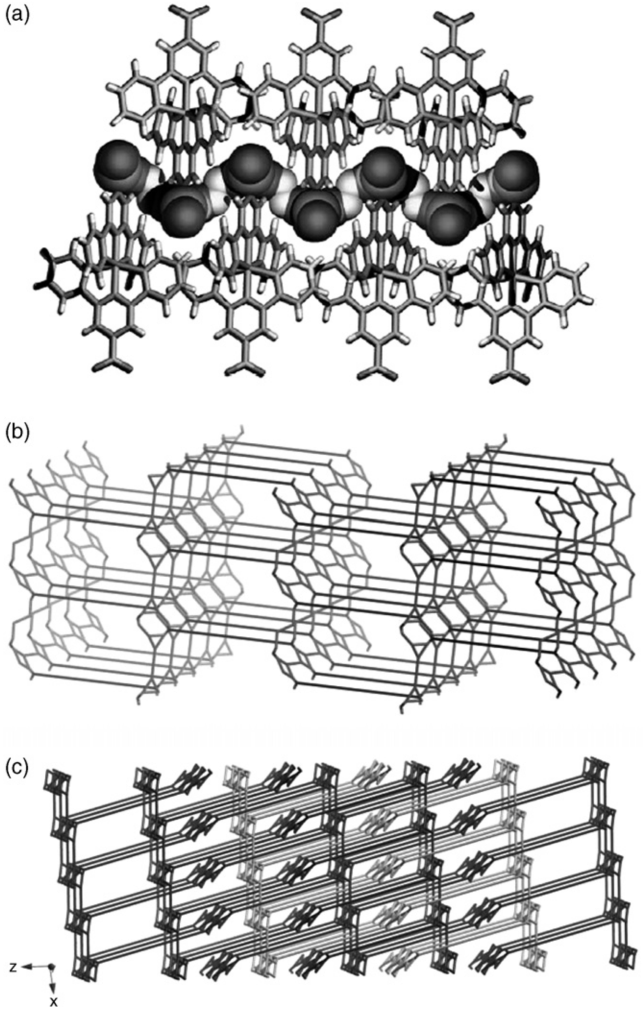
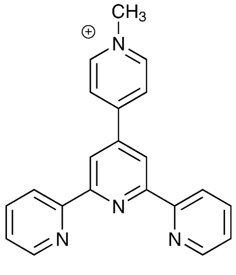


Fig. 7. In the complexes $[Ru(\mathbf{23}\text{-}H)_2]\cdot 4H_2O$ and $[Ru(\mathbf{24}\text{-}H)_2]\cdot 5H_2O$, there are no direct carboxylate–carboxylate interactions, but extensive hydrogen-bonding networks involving carboxylate and water. (a) In $[Ru(\mathbf{23}\text{-}H)_2]\cdot 4H_2O$ the carboxylates and water molecules form a (6.3) network separating the $\{Ru(tpy)_2\}$ motifs. (b) In $[Ru(\mathbf{23}\text{-}H)_2]\cdot 5H_2O$, interpenetrating three-dimensional nets are observed [8].

complexes of 2,2′:6′,2″-terpyridine-4-carboxylic acid **23** and 4′-carboxyphenyl-2,2′:6′,2″-terpyridine **24** [8]. The ruthenium complexes $[Ru(\mathbf{23}\text{-}H)_2]\cdot 4H_2O$ and $[Ru(\mathbf{24}\text{-}H)_2]\cdot 5H_2O$ are both Zwitterionic with deprotonated carboxylate groups. Accordingly, there are no direct hydrogen-bonding interactions between carboxylic acids but rather extended networks involving lattice water and carboxylate. In the case of $[Ru(\mathbf{23}\text{-}H)_2]\cdot 4H_2O$ the carboxylates and the water molecules form a (6.3) network, the sheets of which separate the $\{Ru(tpy)_2\}$ motifs (Fig. 7a). In the further expanded system $[Ru(\mathbf{24}\text{-}H)_2]\cdot 5H_2O$, a three-dimensional network of carboxylate groups and water molecules is formed (Fig. 7b). The incorporation of the phenylene spacers would result in a very open lattice (Fig. 7b) and a triply interpenetrated structure results (Fig. 7c).



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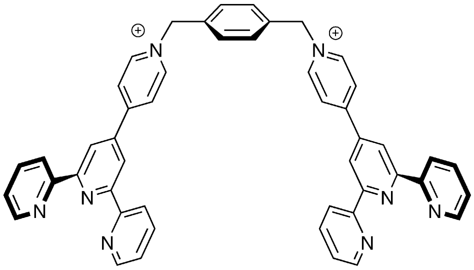

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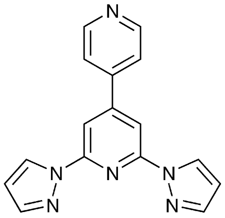

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5. Chemical analogies between expanded ligands incorporating $\{M(tpy)_2\}$ scaffolds and the parent structures

In the preceding sections, the structural analogies between expanded ligands and their parent structures have been established. We now ask whether the *chemical* reactivity of the expanded ligands also resembles that of the parent structures.This section will specifically discuss the reactivity of compounds based upon $\{M(tpy)_2\}$ scaffolds.

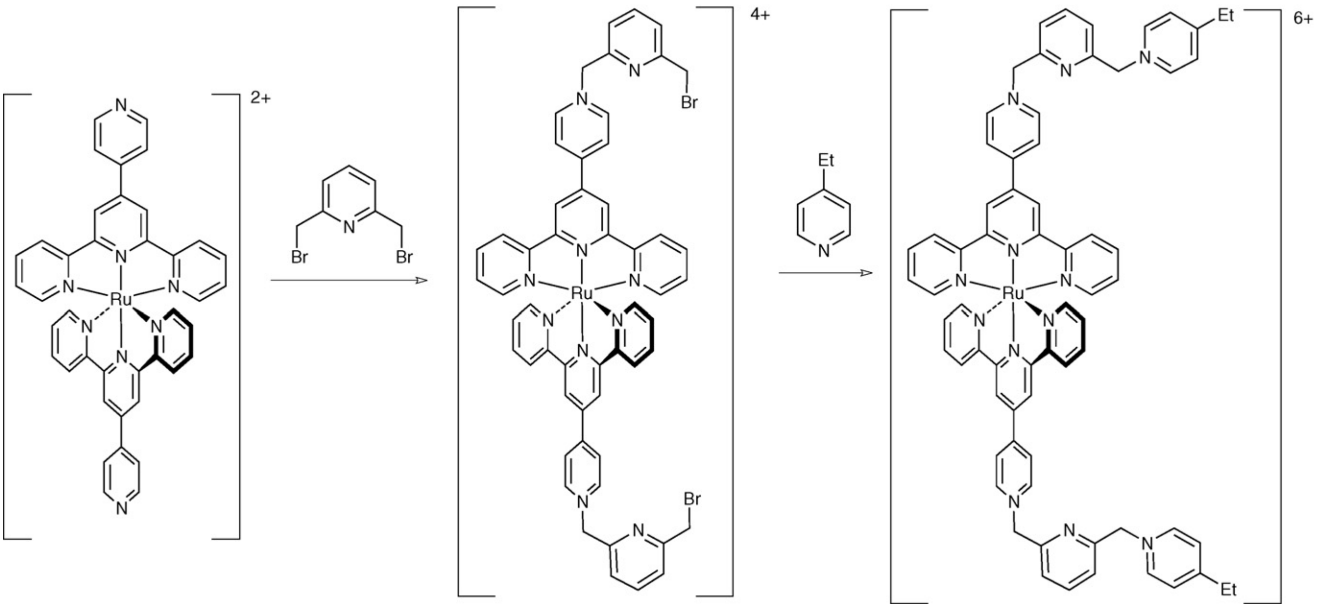
5.1. Expanded bipyridines

In the introductory sections we introduced the analogy between 4,4′-bipyridine (or pyrazine) with $[M(\mathbf{7})_2]^{n+}$ complexes incorporating pendant 4-pyridyl groups. A number of $\{M(\mathbf{7})_2\}^{n+}$ complexes ($n=2$, M = Fe [1,26,50–53] Ru [2,7,51–56], Os [51–53,56], Co [57], Cu [27]; $n=3$, M = Co [58], Rh [28], Ir [59]) have been reported. Analogous iridium(III) complexes with pendant 2,6-dimethylpyridin-4-yl [59] and 4-(4-pyridyl)phenyl [59] substituents have also been described. We and others have demonstrated that the reactivity of the pendant 4-pyridyl substituents strictly parallels that of 4,4′-bipyridine and that it is possible to protonate [50,51], alkylate [1,2,26,50,51] and coordinate additional metal ions [3,52–54] at these positions.As expected, the positive charge on the $[M(\mathbf{7})_2]^{n+}$ complexes reduces the basicity of the pendant pyridine nitrogen as seen in a comparison of pK_{a1} for 4,4′-bipyridine (4.8) [60] with $[M(\mathbf{7})_2]^{2+}$ (M = Fe, 2.9 [50], M = Ru, 4.5 [61], M = Os, 4.6 [61]). We have discussed in detail the effect of protonation on the photophysical properties of these complexes and the variations in pK_a between the excited and ground states [61].

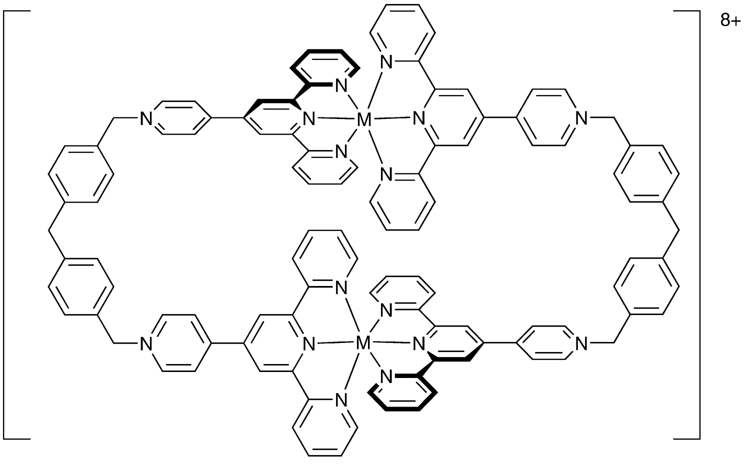
The pendant 4-pyridyl groups are readily alkylated—in the case of $[Fe(\mathbf{7})_2]^{2+}$ the conversion to $[Fe(\mathbf{25})_2]^{4+}$ is accompanied by a spectacular and beautiful colour change from purple to royal blue [50]. It is possible to incorporate highly functionalised substituents through the alkylation reactions and to perform subsequent transformations to obtain novel supramolecular species (Scheme 1) [26]. Kurth has extended this methodology to the preparation of metallopolymers and has shown demonstrated that the alkylation methodology may be used for the preparation of electrochromic polymers based upon the cationic bridging ligand **26** [62–65].

To what extent do the reactions of $\{M(\mathbf{7})_2\}^{n+}$ complexes really parallel those of 4,4′-bipyridine? One of the dominant features in the chemistry of 4,4′-bipyridine is the formation of a rich array of 1-, 2- and 3D coordination polymers and networks (430 examples in the CSD). One of the simplest structural motifs is found in monoprotonated salts of 4,4′-bipyridine in which one-dimensional chains of 4,4′-bipyridines are linked by protons with N···N distances in the range 2.6–2.7 Å [66–82] and we have recently reported the first examples of this motif in expanded ligands in $[Fe(\mathbf{7})(H\mathbf{7})]^{3+}$ complexes (Fig. 8) [5]. We note that the compound reported in the literature [28] as $[Rh(\mathbf{7})_2][PF_6]_3$ has N···N distances between the pendant 4-pyridyl groups of 2.653 Å (c.f. 2.625–2.684 Å in $[Fe(\mathbf{7})(H\mathbf{7})]^{3+}$ salts) and we propose that this compound should be reformulated as a salt of $[Rh(\mathbf{7})(H\mathbf{7})]^{4+}$ with the disordered solvent being better modelled as an additional anion. This same one-dimensional motif has also been recently reported in the complex $[Fe(\mathbf{27})(H\mathbf{27})][ClO_4]_3$ with the structurally analogous ligand **27** [83].

A strict analogy between 4,4′-bipyridine and $[M(\mathbf{7})_2]^{2+}$ (M = Fe, Ru) salts is also established in the preparation of metallomacrocycles of the type **28**. These compounds are analogous to the 4,4′-bipyridine macrocycles **29** reported by Stoddart and co-worker [84]. We have investigated routes to the compounds involving the coordination of the cationic bridging ligand **30** (prepared by alkylation of **7** with **31**) to labile metal ions or the alkylation of $[M(\mathbf{7})_2]^{2+}$ units with the cap **31** [1,2]. These compounds make a conceptual and actual bridge between alkylation and the coordination chemistry of the extended ligand. The effectiveness of the two strategies depends upon the metal ions used and iron(II) and ruthenium(II) compounds behave differently.



Scheme 1. Alkylation of 4,4′-bipyridine expanded ligands is a powerful methodology for the preparation of highly functionalised metallosupramolecules [26].



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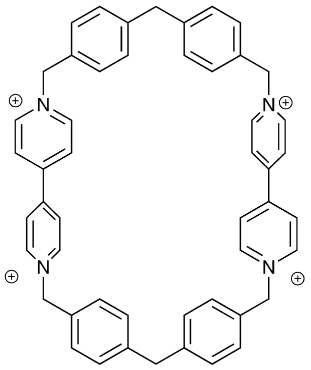

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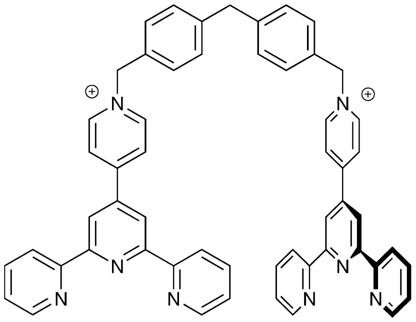

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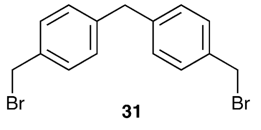

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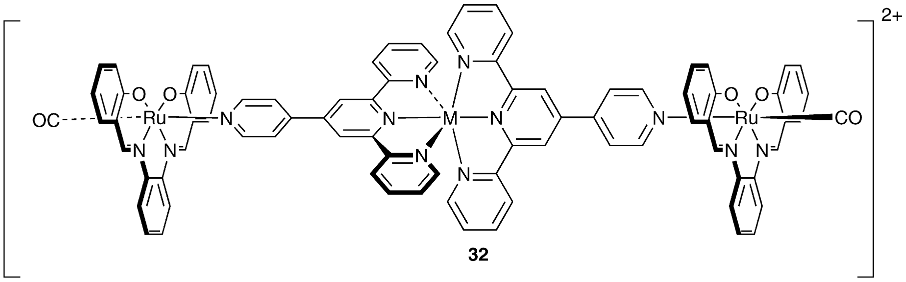

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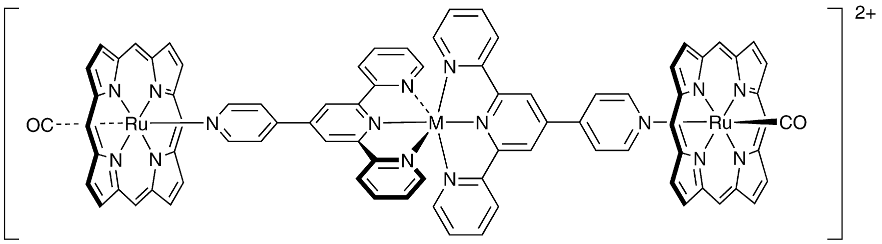

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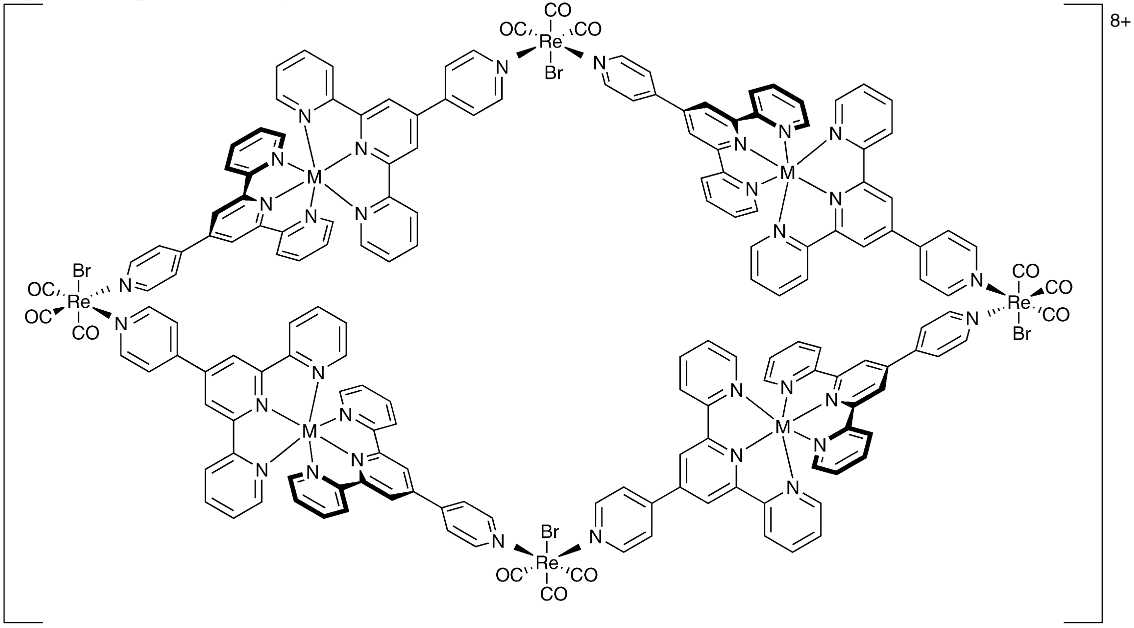
Two examples of simple trinuclear complexes derived from $\{M(\mathbf{7})_2\}^{n+}$ have been described, involving the coordination of carbonyltetraarylporphyrinruthenium **32** [55] or carbonylsalophenruthenium **33** [57] units to the nitrogen donors of the pendant 4-pyridyl groups. The pioneering work of Fujita, Stang and others in the self-assembly of molecular polygons and polyhedra by the interaction of vectorially defined bridging ligands with metal-coordination units with preferred coordination geometries relies heavily on 4,4′-bipyridine and related compounds [85–89] and it might be expected that analogous compounds with $\{M(\mathbf{7})_2\}^{n+}$ motifs replacing 4,4′-bipyridine could be prepared. To date, only one system such has been reported [52,53] in which four $\{Re(CO)_3Br\}$ corners are connected by four $\{M(\mathbf{7})_2\}$ bridges (M = Fe, Ru, Os) to give the octanuclear species **34**. Detailed photophysical studies of these compounds have been reported and the analogy to 4,4′-bipyridine squares is firmly established.

Perhaps most remarkably, until recently there were no examples of one-dimensional polymers constructed from $\{M(\mathbf{7})_2\}^{n+}$ units connected by coordination of the pendant 4-pyridyl donors to other metal centres. This is somewhat surprising in view of the ubiquitous use of 4,4′-bipyridine as a bridging ligand in crystal engineering. We have recently described the first example of such a compound in which $[Ru(\mathbf{7})_2]^{2+}$ expanded ligands are connected by $Ag(NO_3)(MeCN)$ moieties (Fig. 8c) [3]. The compound is simply prepared from the reaction of $[Ru(\mathbf{7})_2]^{2+}$ with $AgNO_3$ in acetonitrile. Although no simple 4,4′-bipyridine polymer based on silver(I) has been structurally characterized a very similar 1D chain is found in a silver(I) pyrazine 1,3,6,8-pyrenetetrasulfonate complex (Fig. 8d) [90]. In both compounds the Ag–N distances are in the range 2.2–2.3 Å although the chain in the expanded ligand complex is less linear (∠N–Ag–N 150°)



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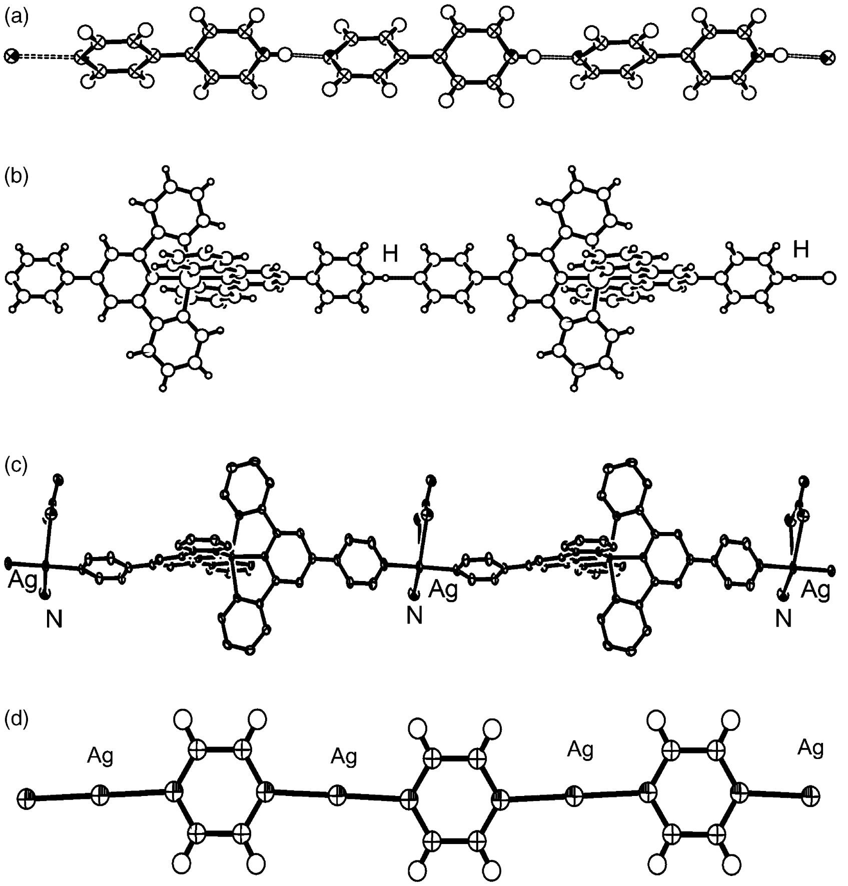


Fig. 8. The 1D hydrogen-bonded motifs present in (a) the salt 4,4′-bipyridinium chloro(dicyanoethene-1,2-dithiolato)dimethylstannate(IV) [66] and (b) in the expanded ligand $[\mathrm{Fe}(\mathbf{7})(\mathrm{H}\mathbf{7})][\mathrm{ClO_4}]_3$ [5]. (c) The 1D coordination polymer present in $[\mathrm{Ru}(\mathbf{7})_2\mathrm{Ag}(\mathrm{NO_3})(\mathrm{MeCN})](\mathrm{NO_3})_2$ with only the acetonitrile nitrogen donor shown and (d) the analogous 1D-chain in a silver(I) pyrazine 1,3,6,8-pyrenetetrasulfonate complex [90].

than in the pyrazine derivative (∠N–Ag–N, 172°, 179°). The above discussion clearly establishes the utility of the expanded ligand concept and demonstrates that the solid state chemistry of these species genuinely parallels that of the prototype ligands.

Complexes of isomeric 3-pyridyl- and 2-pyridyl-2,2′:6′,2″-terpyridines **8** and **9** are unfortunately less well studied than those of the 4-pyridyl compound **7**. Only two examples of $\{\mathrm{M}(\mathbf{9})_2\}^{n+}$ complexes have been reported [29,59]. The photophysical properties of the isomeric complexes $[\mathrm{IrL_2}]^{3+}$ (L = **7**, **8** or **9**) have been studied in detail [59]. However, most relevant to this discussion are the copper complexes obtained from hydrothermal reactions of **9** with CuI and KI [28]. Amongst the suite of products isolated from these reactions is the mixed oxidation state compound $[\mathrm{Cu_2}(\mathbf{7})_2\mathrm{I_2}][\mathrm{Cu}(\mu\text{-I})\mathrm{I}]$. This salt contains a discrete mixed oxidation state cation comprising a $\{\mathrm{Cu^{II}}(\mathbf{7})_2\}$ moiety in which one of the 2-pyridyl substituents is coordinated to a $\{\mathrm{Cu^{I}I_2}\}$ unit (Fig. 9). The most significant interionic interactions are weak I···H–C hydrogen bonds and to date no extended structures incorporating **9** have been reported.

The extended ligands $\{\mathrm{M}(\mathbf{8})_2\}^{n+}$ with the 3-pyridyl ligand have also received very little attention and until recently the only compounds reported were $[\mathrm{Ru}(\mathbf{8})_2][\mathrm{PF_6}]_2$ [6] and $[\mathrm{Ir}(\mathbf{8})_2][\mathrm{PF_6}]_3$ [59]. Very recently an extended structures have been obtained from the reaction of $[\mathrm{Ru}(\mathbf{8})_2]^{2+}$ with silver(I) salts and the complex has been characterized as polymeric network consisting of a layered non-interpenetrating set of elongated (6.3) nets (Fig. 10) [31].

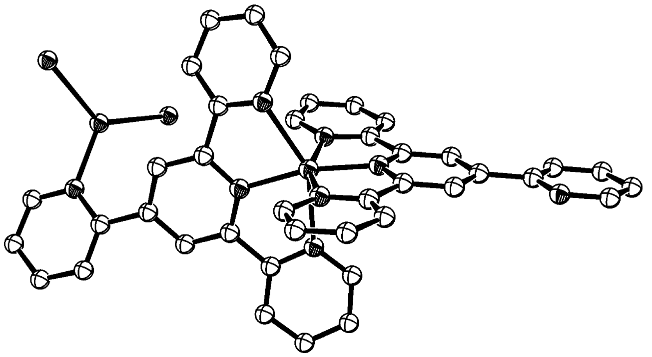


Fig. 9. The discrete $[\mathrm{Cu^{II}}(\mathbf{7})_2\mathrm{Cu^{I}I_2}]^+$ cation present in the 4′-(2-pyridyl)-2,2′:6′,2″-terpyridine complex $[\mathrm{Cu_2}(\mathbf{7})_2\mathrm{I_2}][\mathrm{Cu}(\mu\text{-I})\mathrm{I}]$ [28].

5.2. Expanded phthalic acids

There are only two reports of homoleptic complexes of 2,2′:6′,2″-terpyridine-4′-carboxylic acid complexes **23**, both involving the ruthenium complex **10** [8,91]. The preparation of the complexes is not trivial and the best procedures involve oxidation of the substituents in precursor complexes $[\mathrm{Ru}(\mathbf{35})_2]^{2+}$ with the 4′-(2-furyl)-2,2′:6′,2″-terpyridine ligand

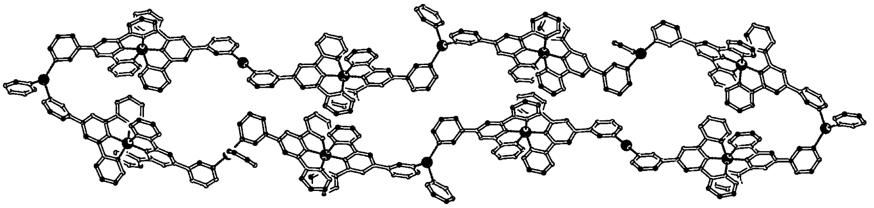
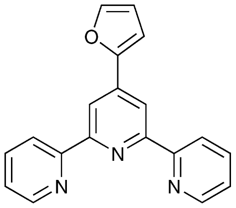


Fig. 10. The interaction of silver with $[\mathrm{Ru}(\mathbf{8})_2]^{2+}$ leads not to a 1D linear polymer but to a layered 2D structure. This is a consequence of the non-linearity of the N···Ru···N vector and part of the resultant (6.3) net is shown [31]. Only the 3-pyridyl rings of the cations that extend the network are shown.

35 rather than direct coordination of **22**. In all cases, the precise products isolated depend upon the reaction conditions and it is possible to obtain any of the three compounds $[\mathrm{Ru}(\mathbf{23})_2]^{2+}$, $[\mathrm{Ru}(\mathbf{23})(\mathbf{23}\text{-H})]^{+}$ or $[\mathrm{Ru}(\mathbf{23}\text{-H})_2]$. In our hands, all attempts to prepare expanded ligand analogues of the Yaghi-type metal–organic-frameworks [92] have only yielded the parent ruthenium complexes in various protonation states. The structural chemistry of these species is of interest and is discussed in Section 4 above [8]. The further expanded complex **11** has been studied by a number of groups [8,93,94] and aspects of the solid state chemistry are again discussed in Section 4. Once again, we have been unable to obtain any metal–organic-frameworks using this expanded ligand.



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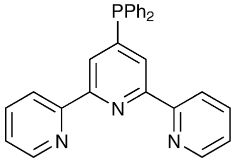
5.3. Expanded polyphosphines

Phosphine ligands play a central role in coordination chemistry and the contrast of the soft nature of the phosphorus donor(s) and the harder tpy metal-binding domains makes hybrid tpy–phosphine ligands of interest. In particular, the presence of discrete hard and soft domains should allow selective addressing of the phosphine or tpy domains. Two examples of expanded ligands of this type have been reported, the first being ligand **36** which forms complexes $\{\mathrm{M}(\mathbf{36})_2\}$ that can be regarded as diphosphine analogues [95–97] and the second is the dppm derivative **37** which gives $\{\mathrm{M}(\mathbf{37})_2\}$ complexes that are expanded tetraphosphines [98]. Both ligands can be selectively addressed at the phosphine donors with soft metals such as palladium(II) or platinum(II) or at the tpy metal-binding domains with harder metals such as iron(II), cobalt(II), ruthenium(II) or osmium(II). The complexes $[\mathrm{M}(\mathbf{36})_2]^{2+}$ (M = Fe, Ru) have been shown to act as diphosphine analogues and the discrete species $[\mathrm{M}(\mathbf{36})_2\mathrm{X}_2]$ (M = Fe, Ru; X = W(CO)$_5$, Mo(CO)$_5$, Os$_3$(CO)$_{11}$) in which the metal-carbonyl moiety is coordinated to the pendant phosphine donors have been characterized [95,96].



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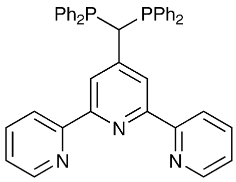

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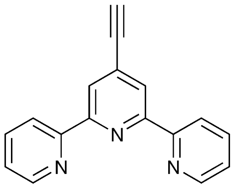
5.4. Expanded polyacetylenes

The principle of functionalizing the harder tpy metal-binding domains with softer donors is a logical one in developing regiospecific heterotopic ligands and a second set that has proved of interest is the C-donor of an acetylide. A significant number of tpy–alkyne conjugates are known, but those that fall strictly within the expanded ligand category with a $\{\mathrm{M}(\mathrm{tpy})_2\}$ core and extrinsic alkynes are limited to complexes of ligands **38**–**40**. The homoleptic complexes $[\mathrm{Ru}(\mathbf{38})_2]^{2+}$ [99,100], $[\mathrm{Cu}(\mathbf{38})]^{2+}$ [101], $[\mathrm{Fe}(\mathbf{39})_2]^{2+}$ [24] and $[\mathrm{Ru}(\mathbf{40})_2]^{2+}$ [102–104] have been reported.



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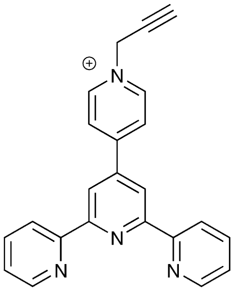

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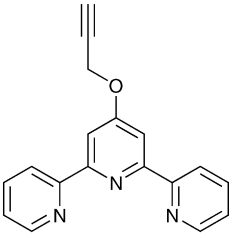

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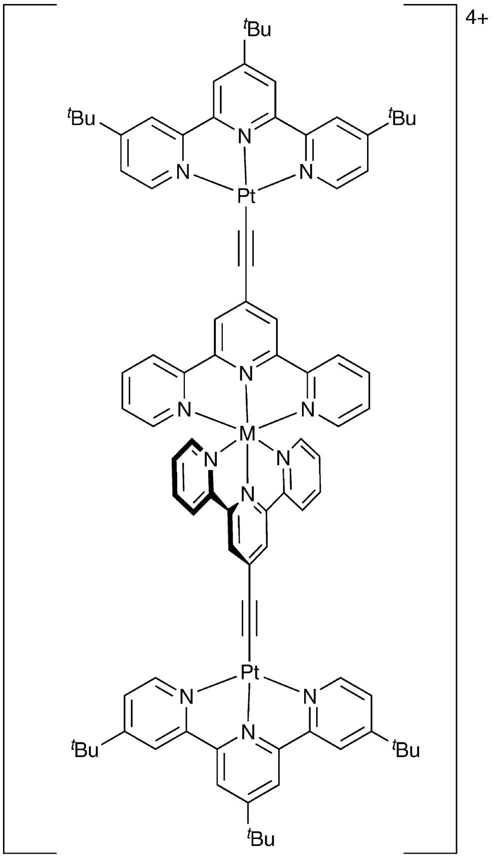
The complexes behave as typical bis(alkynes) and Ziessel has demonstrated the reaction at the terminal CH groups of $[\mathrm{Ru}(\mathbf{38})]^{2+}$ to give trinuclear complexes with capping 4,4′,4″-tris(*tert*-butyl)-2,2′:6′,2″-terpyridineplatinum(II) capping groups **41** [105] whereas we have shown that the alkyne groups retain their characteristic reactivity in $[\mathrm{Ru}(\mathbf{40})_2]^{2+}$ and undergo typical cluster-forming reactions with Co$_2$(CO)$_8$ to form the cluster-functionalised pentanuclear complex **42** [102,104].



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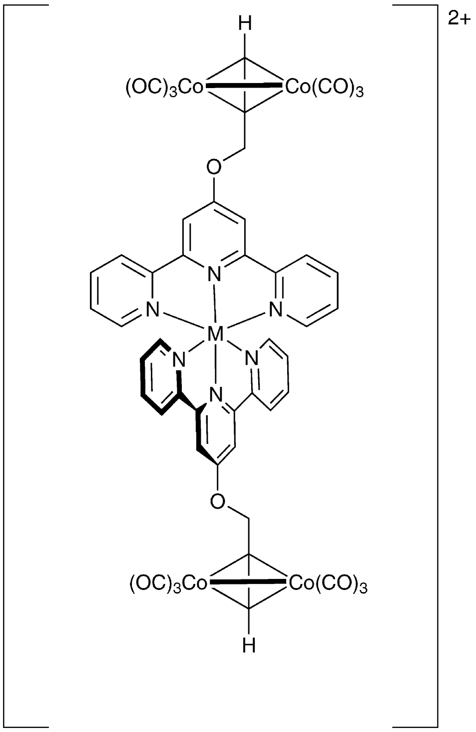

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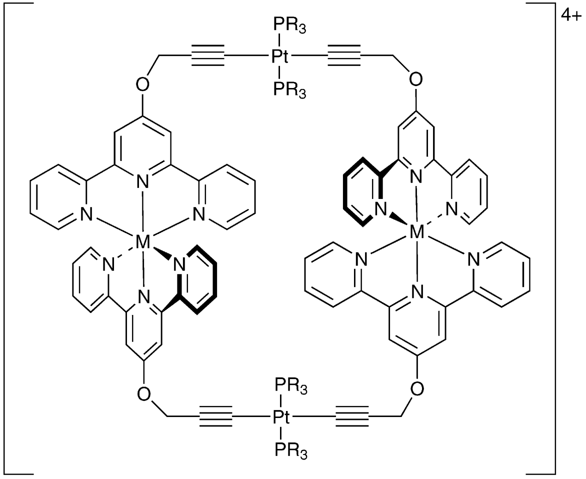
Finally, we have shown that the expanded ligand concept applies to the formation of metallomacrocycles of type **43** from derivatives of **40** [106]. In the prototype reactions we used a self-assembly process for the assembly of the expanded ligand motif and obtained the macrocycle **43** (R = *n*-butyl, M = Fe) from the reaction of iron(II) salts with [Pt(PR_3)$_2$(**40**-H)$_2$] in good yield [86] and more recently we have studied the assembly of these species in detail and investigated the speciation as a function of the phosphine used [107].



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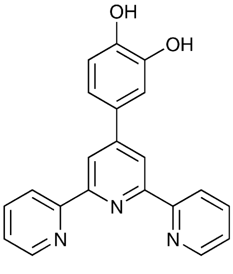
5.5. Expanded polycatechols

Another popular ligand class involves the *O,O′*-donor set of catecholates and expanded ligands incorporating this motif have been reported by Ward and co-workers [108,109] and Abruña and co-workers [110]. The compounds [M(**44**)$_2$]$^{2+}$ (M = Fe [110], Co [109,110], Cr [110], Zn [109], Ru [108–110]) have been described and the electrochemical behaviour investigated in detail [110]. The ability to act as an expanded ligand has been established by Ward who has prepared the compound **45** [108].



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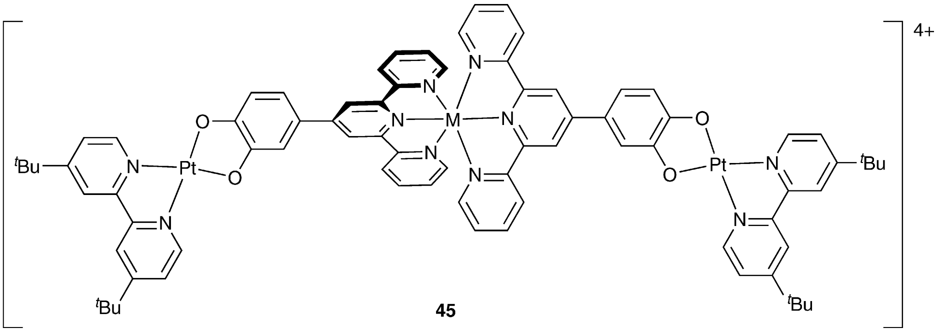

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6. Closing remarks

In this article, I have presented the concept of expanded ligands and presented evidence to support the validity of the principle. Although the article concentrated upon $\{M(tpy)_2\}$ motif, the concept is general and I believe it will have wide application in supramolecular chemistry and crystal engineering.

Acknowledgements

I would like to thank all of the talented co-workers who have worked in the Constable-Housecroft research group over the years who have performed the chemistry that has allowed us to develop these structural and functional models. I would also like to thank the University of Otago for the award of a William Evans Visiting Fellowship, during the tenure of which this article was written.

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