

# 18 Supramolecular coordination chemistry

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Highlights include the formation of the first uranyl-based metallamacrocycles, the assembly of chiral metallocycles containing as many as 47 metal centres by cyclization of metal- and ligand-terminated oligomers under kinetic control, the formation of mesoscopic molecular polygons and capsules that can enantioselectively bind guests, and architectures that ‘self-select’ from a dynamic combinatorial library. Additionally, structural control on the nanomolecular scale has been demonstrated by the formation of a number of polyoxometalate systems including the self-assembly of the polyoxotungstate wheel,  $\{W_{40}\}^{24-}$ , and development of a highly charged nano-container capsule with 20 nanosized pores and channels which allow the entrance of cations like Pr and  $Li^+$ . Finally, a high-nuclearity “Celtic-Ring” isopolyoxotungstate,  $[H_{12}W_{36}O_{120}]^{12-}$ , that captures trace potassium ions, has been discovered.

## 1. Introduction and scope

This report focuses on the development in design, synthesis and self-assembly of metallosupramolecular-based architectures and ligands designed to aid their construction. The pace of modern crystallographic analysis using area detectors is greatly accelerating the discovery of new clusters and supramolecular architectures *etc.* This account is therefore necessarily highly selective. Many crystal structure pictures have been included to aid in the visualisation and conceptualisation of the many interesting metallosupramolecular architectures that have been constructed. A common colour scheme/size scheme is used in all the structural figures, unless otherwise stated; carbon atoms are light grey, nitrogen atoms are white, metal ions are large black spheres, sulfur atoms are large grey spheres, and oxygen or phosphorus atoms are small black spheres.

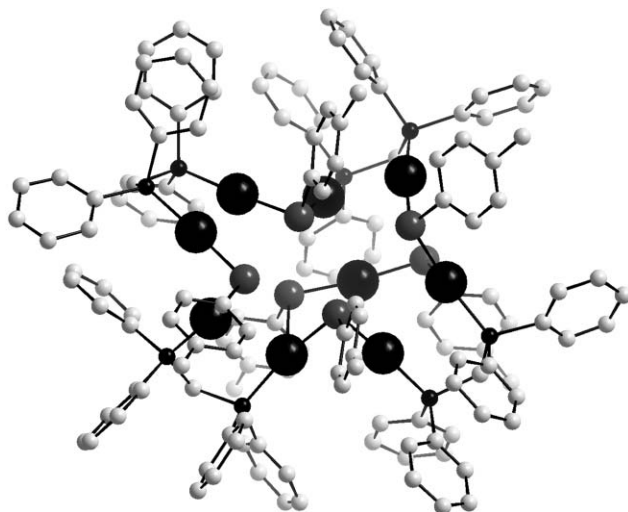
## 2. Metallamacrocycles

The structure of the metallamacrocyclic phosphine Au(I) thiolate cluster  $[Au_9(L^1)_4(L^2)_6](PF_6)_3$ , where  $L^1 = \text{dppm}$  and  $L^2 = \text{para-thiocresolate}$ , has been reported. This cluster supports  $Au \cdots Au$  attractions of *ca.* 3.0 Å, whereby the gold(I) atoms are linked to thiolate and phosphine ligands in distorted trigonal and nearly linear geometries (Fig. 1).<sup>1</sup>

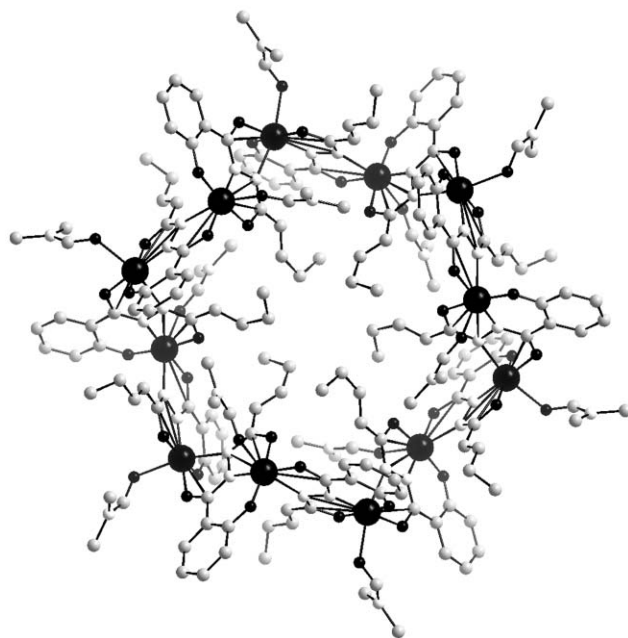
Structural, magnetic and theoretical studies on an octanuclear chromium(III) wheel,  $\{Cr_8\}$ , containing hydroxide and pivalate bridges have been discussed.<sup>2</sup> An interesting dodecanuclear manganese metalladiazamacrocycle was synthesized, employing a new pentadentate ligand *N*-2-pentenoylsalicylhydrazide,  $H_3L^3$ . The backbone of this metal–organic assembly is a repeating M–N–N–M linkage that

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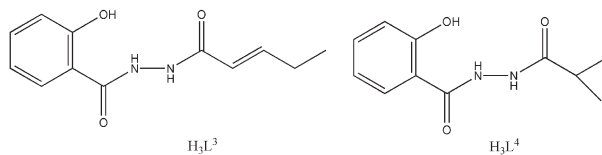


**Fig. 1** Structure of the  $\{\text{Au}_9\}$  cluster. The gold atoms are shown as large black spheres and the sulfur atoms as dark grey spheres.



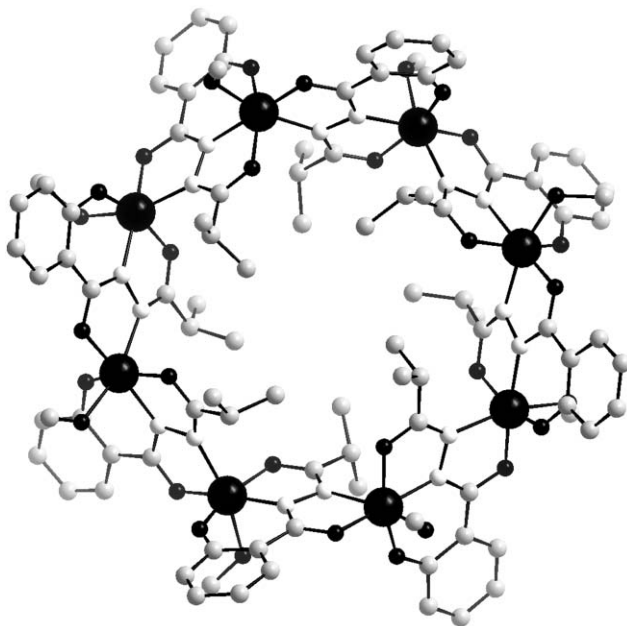
**Fig. 2** A representation of the structure of  $[\text{Mn}_{12}(\text{L}^3)_{12}(\text{dmf})_{12}]$ . The Mn atoms are shown as large black spheres.

extends to complete a 36-membered cyclic structure involving 12 manganese(III) centres (Fig. 2). Successive manganese centres are in chemically different ...ABABAB...-type environments, while the chirality varies in the manner ... $\Lambda\Lambda\Delta\Delta\Lambda\Lambda$ .... The unique arrangement of manganese centres results in a highly puckerd metalladiazamacrocyclic with a  $S_6$  point group symmetry.<sup>3</sup>

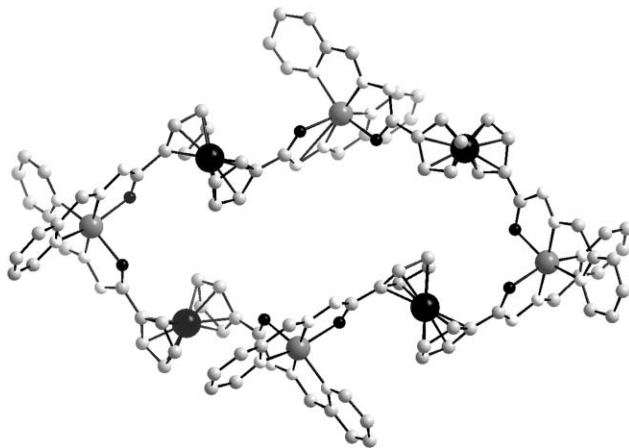


A new pentadentate *N*-isobutyrylsalicylhydrazidate ligand,  $\text{H}_3\text{L}^4$ , was used in the self-assembly of the first 24-azametallacrown-8,  $[\text{Fe}_8(\text{L}^4)_8(\text{CH}_3\text{OH})_8]$ , (Fig. 3). Eight Fe(III) ions and eight deprotonated  $\text{L}^4$  ligands construct a planar, 24-membered ring, based on the M–N–N–M linkage.<sup>4</sup> The chiralities of the iron atoms on the 24-azametallacrown-8 ring alternate between the  $\Lambda$  and  $\Delta$  forms. The octanuclear azametallacrown has no crystallographic centrosymmetry, whereas all of the other known metallacrowns and azametallacrowns with an even nuclear number of metal atoms have crystallographic centrosymmetry.  $^1\text{H}$  NMR spectra indicate that the title compound retains its metallacrown structure in solution at room temperature. There is also a strong antiferromagnetic exchange interaction between the iron centres.

The reaction of  $[\text{Fe}_3\text{O}(\text{PhCOO})_6(\text{H}_2\text{O})_3]\text{NO}_3$  with 1,1,1-tris(hydroxymethyl)ethane,  $\text{H}_3\text{L}^5$ , affords either the octametallic species  $[\text{Fe}_8(\text{PhCOO})_{12}(\text{L}^5)_4]$  or the hexadecametallac species  $[\text{Fe}_{16}(\text{EtO})_4(\text{PhCOO})_{16}(\text{HL}^5)_{12}](\text{NO}_3)_4$ , depending on the nature of the solvent used for crystallization.<sup>5</sup> The  $\{\text{Fe}_8\}$  cluster can be described as a non-planar wheel of eight Fe(III) ions bridged by a combination of  $\text{PhCOO}^-$  and  $(\text{L}^5)^{3-}$  ligands, and the  $\{\text{Fe}_{16}\}$  cluster as a non-planar wheel of sixteen Fe(III) ions bridged by  $\text{PhCOO}^-$ ,  $(\text{HL}^5)^{2-}$  and  $\text{EtO}^-$  ligands. Density functional theory calculations show that the antiferromagnetic interactions between the metals in the dinuclear units decrease when two types of bridging ligand are present, as expected for an orbital counter-complementarity effect. The reactions of the ligands

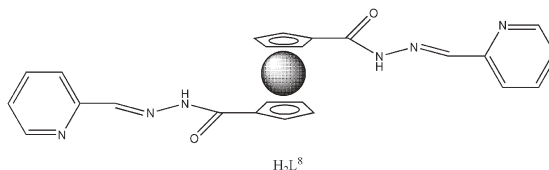


**Fig. 3** A representation of the structure of  $[\text{Fe}_8(\text{L}^4)_8(\text{CH}_3\text{OH})_8]$ . The Fe atoms are shown by the black spheres.

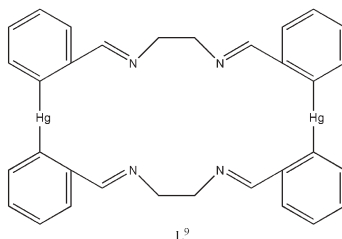


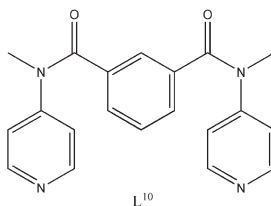
**Fig. 4** A representation of the structure of  $\text{Ni}_4\text{L}^8$ ; a  $\{\text{Ni}_4\text{Fc}_4\}$ -based macrocycle. The Fe and Ni atoms are shown as the large black and dark grey spheres respectively.

*N*-methyldiethanol amine and *N*-ethyldiethanol amine (abbreviated  $\text{H}_2\text{L}^6$  and  $\text{H}_2\text{L}^7$  respectively) with  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]$  yield novel dodecanuclear wheel-shaped products. Ligands  $\text{H}_2\text{L}^6$  and  $\text{H}_2\text{L}^7$  have also been used to form a new hexanuclear ferric wheel.<sup>6</sup> An octanuclear macrocyclic compound,  $\text{Ni}_4\text{L}^8$ , was constructed *via* self-assembly from  $\text{Ni}(\text{BF}_4)_2$  and the ferrocene-containing bis(tridentate) ligand,  $\text{H}_2\text{L}^8$ . The compound exhibits a channelled structure with cavities inside, and can sense the presence of  $\text{Mg}^{2+}$  electrochemically in the solid state (Fig. 4).<sup>7</sup>

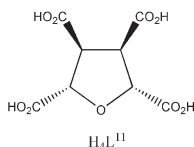


Trinuclear Cu(I) and Ag(I) pyrazolates  $\{[3,5-(\text{CF}_3)_2\text{Pz}]\text{M}\}_3$  ( $\text{M} = \text{Cu}$  and  $\text{Ag}$ ) react with pyridazine to give neutral, tetranuclear metallacycles with a *para*-cyclophane core; whereas benzo[*c*]cinnoline fails to break the cyclic pyrazolate trimers under similar conditions, and instead affords a metallapropellane featuring both two- and three-coordinate metal sites.<sup>8</sup> A metallamacrocycle that contains both a Lewis acidic mercury centre and basic nitrogen atoms in a reorganised macrocycle has been synthesized ( $\text{L}^9$ ). This takes the form of a cationic complex of a mercuramacrocycle that exhibits metallophilic interactions between the coordinated Cu(I) and Hg(II) centres and aggregates in the solid state *via*  $\text{Hg}\cdots\text{Hg}$  interactions (Fig. 5).<sup>9</sup>

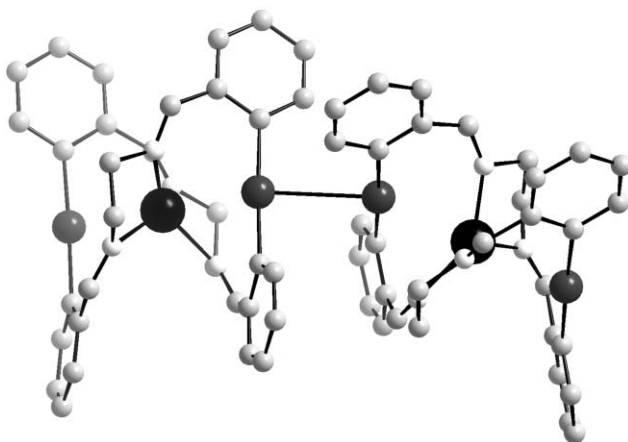




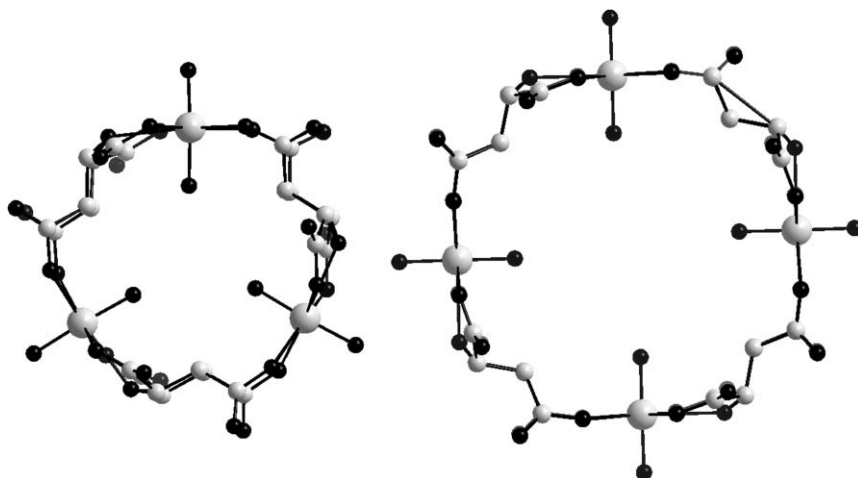
Reaction of the *N*-methylated bis(amidopyridine) ligand,  $L^{10}$ , with silver salts gave the corresponding cationic disilver(I) macrocycles  $[Ag_2(\mu-L^{10})_2]X_2$ . The transannular  $Ag \cdots Ag$  distance in the macrocycles varies greatly between 2.99 and 7.03 Å in different salts due to a combination of different modes of anion binding and the presence or absence of  $Ag \cdots Ag$  secondary bonding.<sup>10</sup> The first uranyl-based metallamacrocycles have been formed in basic solution from the tetra-acid  $H_4L^{11}$ . By controlling the base used to deprotonate the tetra-acid ligand, either trinuclear  $[UO_2L^{11}]_3^{6-}$  or tetranuclear  $[UO_2L^{11}]_4^{8-}$  is formed (Fig. 6).<sup>11</sup> Syntheses of tetra- and hexanuclear uranium(IV) complexes have also been achieved with hexadentate compartmental Schiff base ligands.<sup>12</sup>



An anionic heteronuclear metallamacrocyclic triangle has been produced from the reaction of *trans*- $[Pt\{CM\equiv C(Ar)C\equiv CH\}_2(PMe_3)_2]$  ( $Ar = C_6Me_4-3,4,5,6$ ) with  $PPN[Au(acac)_2]$  ( $Hacac = \text{acetylacetone}$ ,  $PPN = (Ph_3P)_2N$ ), in 1 : 1.16 molar ratio, to give  $PPN [Au\{Pt(PMe_3)_2\}_2\{\mu-Ar(C\equiv C)_2\}_3]$ .<sup>13</sup> Its crystal structure showed the anions to be quasi-equilateral triangles, stacked parallel to each other *via*  $C-H \cdots Au$  interactions, resulting in channels of rhombic cross-section (Fig. 7).

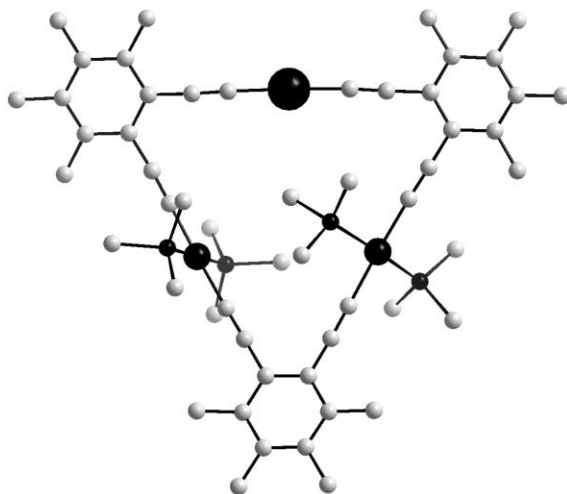


**Fig. 5** A representation of the structure of the macrocyclic complex  $\{CuL^9\}_2$  containing  $Hg(II) \cdots Cu(I) \cdots Hg(II) \cdots Hg(II) \cdots Cu(I) \cdots Hg(II)$  interactions. The Cu and Hg centres are shown in black and dark grey respectively.

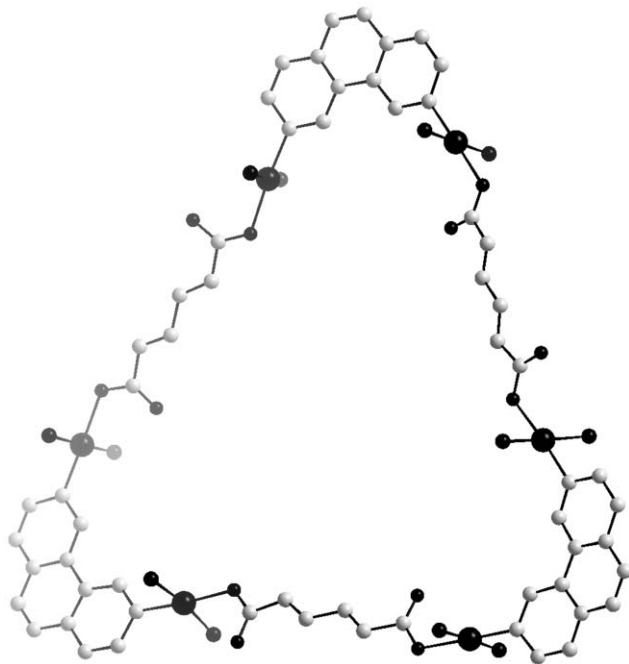


**Fig. 6** A representation of the structures of  $[\text{UO}_2\text{L}^{11}]_3^{6-}$  and  $[\text{UO}_2\text{L}^{11}]_4^{8-}$ . The U atom is shown as large grey spheres.

Several novel metallamacrocycles involving Pt ions have been reported. For instance, the interaction of the 22-membered selenaza macrocycle with Pt(II) leads to the formation of a novel cationic Pt(IV) metallamacrocyclic complex *via* the oxidative addition of a C–Se bond to Pt(II).<sup>14</sup> In other studies, a series of neutral, platinum-based macrocycles were synthesized from rigid oxygen donor building blocks *via* self-assembly. The combination of a platinum-based acceptor unit with several linear and angular dicarboxylate bridging ligands yields neutral, platinum-based, supramolecular triangles and rhomboids; one example being given in Fig. 8.<sup>15</sup> The coordination-driven self-assembly of discrete 2-D macrocyclic species from ambidentate pyridyl–carboxylate-based donor ligands and platinum-containing

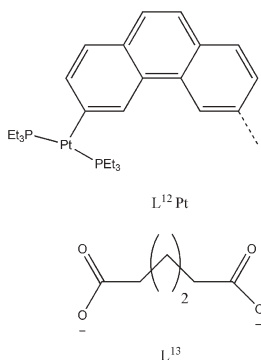


**Fig. 7** A representation of  $[\{\text{Au}\{\text{Pt}(\text{PMe}_3)_2\}_2\}\{\mu\text{-Ar}(\text{C}=\text{C})_2\}_3]^+$ . The Pt and Au atoms are shown as small and large black spheres respectively.

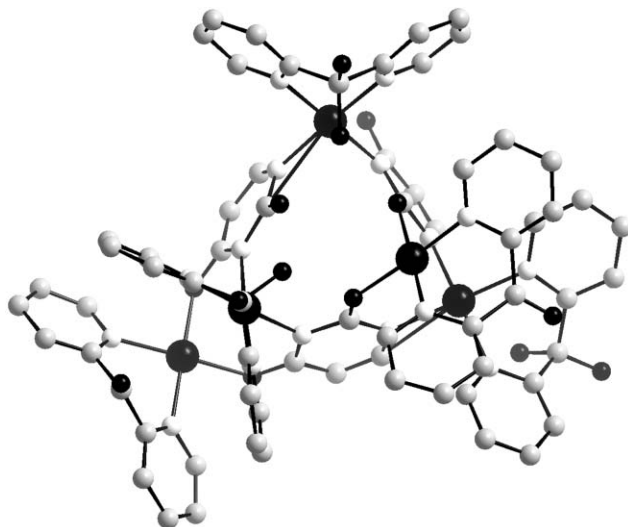


**Fig. 8** Representation of the metallo-triangle  $[\text{Pt}_6(\text{L}^{12})_3(\text{L}^{13})_3(\text{PEt}_3)_6]$ . The ethyl groups of the  $\text{PEt}_3$  units have been omitted. The Pt atoms are shown as the large black spheres.

acceptors has been reported.<sup>16</sup> Chiral molecular squares based on angular bipyridines have also been reported.<sup>17</sup>



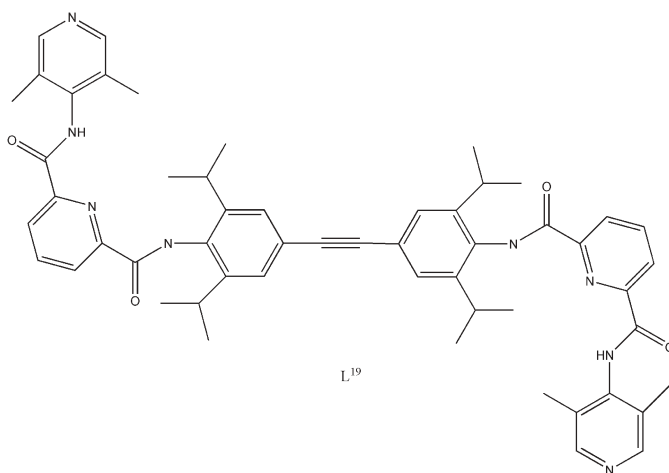
The step-wise, directed assembly of chiral metallocycles containing as many as 47 metal centres by cyclization of metal and ligand terminated oligomers under kinetic control has been reported.<sup>18</sup> These unprecedented mesoscopic molecular polygons, built from 2,2'-diacetoxy-1,1'-binaphthyl-3,3'-bis(ethyne) units,  $\text{H}_2\text{L}^{14}$ , as the bridging ligand and *trans*- $\{\text{Pt}(\text{PEt}_3)_2\}$  units, as the metal connectors, exhibit interesting size-exclusion behaviour. Nanofabrication by reversible self-assembly of an embedded hexameric metallomacrocycle within a macromolecular superstructure is also reported.<sup>19</sup> The first macrocyclic complexes of nucleobases have also been discovered. In this case, three pentanuclear  $\text{Pt}(\text{II})$  macrocycles were prepared by



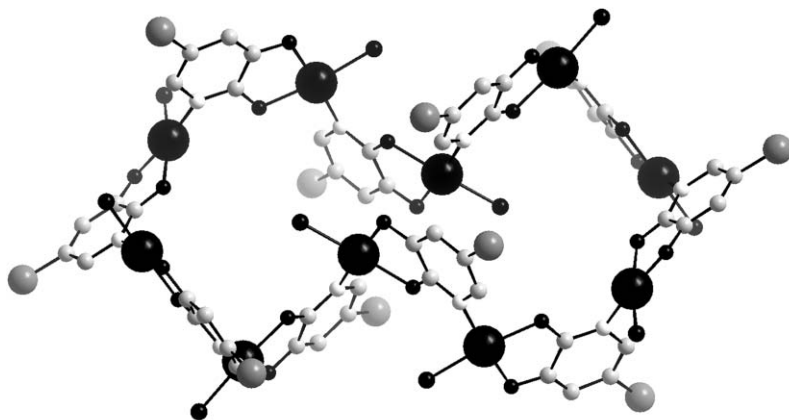
**Fig. 9** The structure of  $[\text{Pt}_5(\text{L}^{15})_2(\text{L}^{16})_3(\text{Ur})_3]^{7+}$ . The Pt atoms are shown as large black spheres.

reaction of a cisplatin analogue with aromatic nitrogen ligands 2,2'-dipyridylketone,  $\text{L}^{15}$ , its hydrate,  $\text{L}^{16}$ , and the nucleobases thymine (T) and uracil (Ur) (Fig. 9).<sup>20</sup>

An unprecedented  $\text{Pd}(\text{I})_8$  crown-cycle with unsupported metal-metal bonds has been formed from the reaction of tri(*N*-pyrrolyl)phosphine,  $\text{L}^{17}$ , with the  $\sigma/\pi$  complex  $[\text{Pd}(\mu\text{-Cl})(\text{COD-MeO})_2]$  to give the octa-cycle  $[\text{Pd}(\mu\text{-Cl})\{\text{L}^{17}\}]_8$ , containing four  $\text{Pd}(\text{I})\text{-Pd}(\text{I})$  unbridged bonds.<sup>21</sup> Complexation of  $\{1,2\text{-bis}(2,2':6',2''\text{-terpyridin-4-yl-ethynyl})\text{benzene}\}$ ,  $\text{L}^{18}$ , with  $\text{Fe}^{2+}$  and  $\text{Ru}^{2+}$  afforded the self-assembled, triangular metallomacrocycles based on  $\{\text{M}(\text{terpy})_2\}^{2+}$  vertices, and possessed a  $60^\circ$  angle between the two terpyridines.<sup>22</sup> Formation of a [2+2]-heterotetranuclear macrocycle by the reaction of a platina-homoditopic ligand with  $\text{Fe}(\text{II})$  has been achieved.<sup>23</sup> A metallamacrocycle in which conjugated terthiophene groups link the metals has also been assembled from a labile Pd complex.<sup>24</sup>



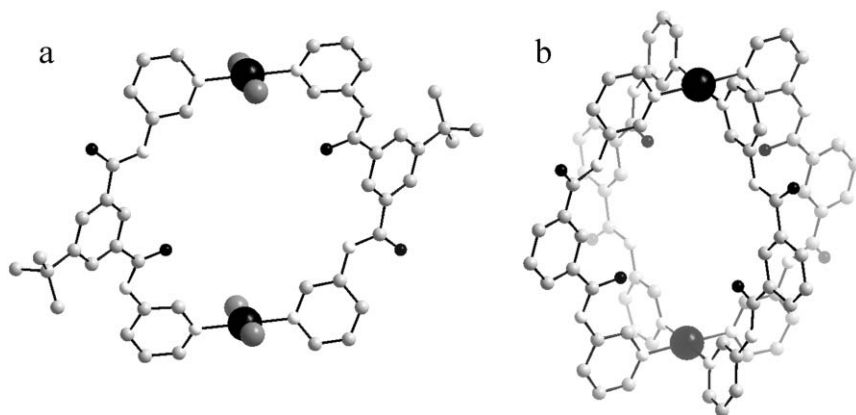




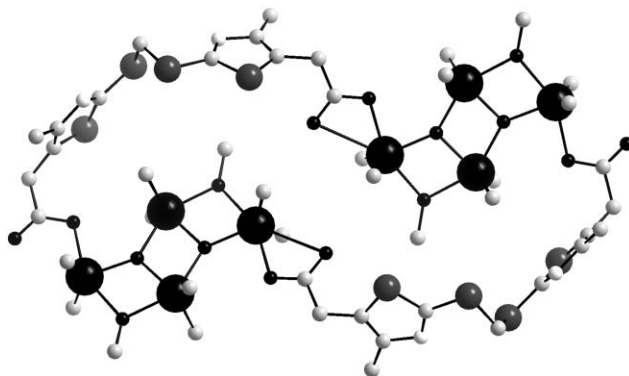
**Fig. 10** A representation of  $[(\text{Et}_3\text{P})\text{Pd}(\text{L}^{21})]_{10}$ . The Pt and Cl atoms are shown by the large black and grey spheres respectively.

Self-assembled metallocycles with two interacting binding domains have been prepared from the S-shaped bis-pyridyl ligand,  $\text{L}^{19}$ , and  $[\text{Pd}(\text{L}^{20})(\text{OTf})_2]$  ( $\text{L}^{20}$  = 1,3-bis(diphenylphosphanyl)propane).<sup>25</sup> The binding properties of metallocycles with *N,N,N',N'*-tetramethylterephthalamide have been probed and evidence for positive cooperativity in the binding found. This cooperativity may be attributed to a structural reorganization of the second binding cavity when the first guest binds to either of the sub-cavities present in the metallocycles. The reaction of  $[(\text{Et}_3\text{P})\text{PdCl}_2]_2$  with 5-chloro-2,3-dihydroxypyridine,  $\text{H}_2\text{L}^{21}$ , in the presence of base gives neutral  $\{\text{Pd}_{10}\}$ -based metallomacrocylic compounds in which the heterocycles act as dianionic bridging ligands (Fig. 10).<sup>26</sup>

The reactions of  $[\text{PdCl}_2(\text{NCPh})_2]$  in a 1 : 1 ratio with the bis(amidopyridine) ligands  $\text{C}_6\text{H}_3(5\text{-R})(1,3\text{-CONH-}3\text{-C}_5\text{H}_4\text{N})_2$  ( $\text{R} = \text{H}$  ( $\text{L}^{22}$ ) or  $\text{R} = \text{'Bu}$  ( $\text{L}^{23}$ )) give the corresponding neutral dipalladium(II) macrocycles, *e.g.*, *trans,trans*- $[\text{Pd}_2\text{Cl}_4(\mu\text{-L}^{23})_2]$ , (Fig. 11a).<sup>27</sup> However, the reaction of  $[\text{PdCl}_2(\text{NCPh})_2]$  with  $\text{L}^{22}$  in a 1 : 2 ratio gives a



**Fig. 11** The structures of a:  $[\text{Pd}_2\text{Cl}_4(\mu\text{-L}^{22})_2]$  and b:  $[\text{Pd}_2(\mu\text{-L}^{23})_4]\text{Cl}_4$  are shown. The Pt and Cl atoms are shown by the large black and grey spheres respectively.



**Fig. 12** The structure of the  $\{\text{Sn}_8\}$  complex. The Sn atoms are shown by the large black spheres.

cationic lantern complex  $[\text{Pd}_2(\mu\text{-L}^{22})_4]\text{Cl}_4$  (Fig. 11b). These lantern complexes exhibit remarkable host–guest chemistry, as they can encapsulate cations, anions, and water molecules by the guest interacting with either the electrophilic NH or the nucleophilic C–O substituents of the amide groups, which can be directed towards the centre of the lantern through an easy conformational change.

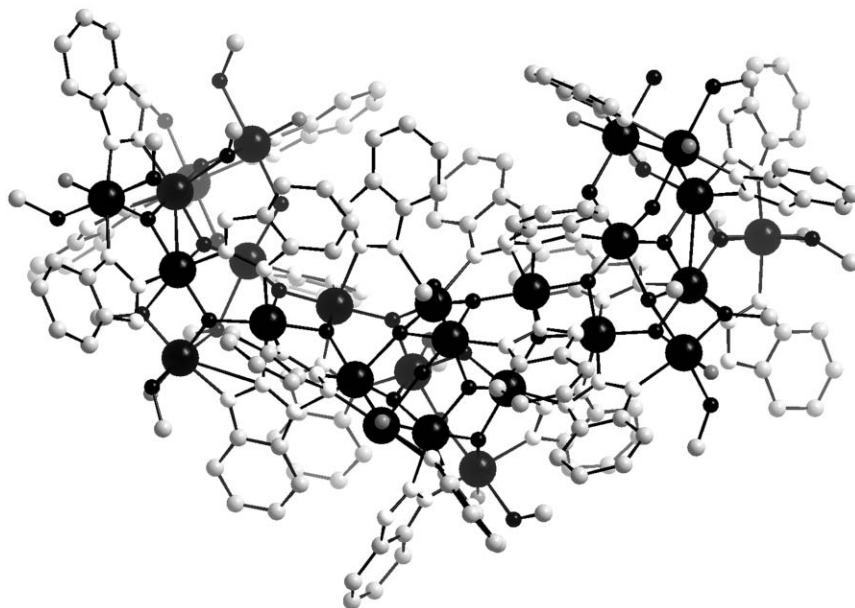
The “weak-link approach” for the synthesis of metallamacrocycles has been used to synthesize a series of novel Ru(II) macrocycles in high yield.  $\text{RuCl}_2(\text{PPh}_3)_3$  was reacted with two different phosphino–alkyl–ether hemilabile ligands, 1,4- $\{\text{PPh}_2(\text{CH}_2)_2\text{O}\}_2\text{C}_6\text{H}_4$ ,  $\text{L}^{24}$ , and 1,4- $\{\text{PPh}_2(\text{CH}_2)_2\text{OCH}_2\}_2\text{C}_6\text{H}_4$ ,  $\text{L}^{25}$ . The hemilabile bidentate ligand coordinates to Ru(II) centres through both the P and O atoms to form bimetallic “condensed intermediates”; the weak Ru–O bonds then selectively cleave with CO, 1,2-diaminopropane or pyridine to yield large, open macrocycles.<sup>28</sup>

Self-recognition in the transition metal mediated self-assembly of 2-D polygons has been reported. Prolonged heating of two or three organoplatinum reagents with 4,4'-dipyridyl in aqueous acetone results in the predominant formation of a rectangle, triangle and/or square.<sup>29</sup> The new ligands 1,1,4,4-tetra(1-pyrazolyl)butane,  $\text{L}^{26}$ , and 1,1,5,5-tetra(1-pyrazolyl)pentane,  $\text{L}^{27}$ , were prepared to determine the structural changes in Ag(I) complexes that accompany the lengthening of the spacer group between two linked bis(pyrazolyl)methane units. These complexes have a cyclic, dimeric structure in the solid state and have extended supramolecular structures based on non-covalent interactions, supported by the counterions and functional groups designed into the ligands.<sup>30</sup>

The self-assembly reaction of 2-mercapto-4-methyl-5-thiazole,  $\text{L}^{28}$ , with acetic acid, sodium methoxide and dimethyltin dichloride in moist dichloromethane affords a novel  $\text{Sn}_8$  complex (Fig. 12) which is a 40-membered macrocycle containing two distannoxane ladders.<sup>31</sup>

### 3. Cluster frameworks and cages

The syntheses, structures and magnetic properties of three new Mn(III) clusters  $[\text{Mn}_{26}\text{O}_{17}(\text{OH})_8(\text{OMe})_4\text{F}_{10}(\text{L}^{29})_{22}(\text{MeOH})_{14}(\text{H}_2\text{O})_2]$  (which shows single molecule magnet (SMM) type behaviour at low temperature),  $[\text{Mn}_{10}\text{O}_6(\text{OH})_2(\text{L}^{29})_8(\text{py})_8\text{F}_8]$  and  $[\text{NHEt}_3]_2[\text{Mn}_3\text{O}(\text{L}^{29})_6\text{F}_3]$  have been reported ( $\text{L}^{29}$  = anion of benzotriazole),

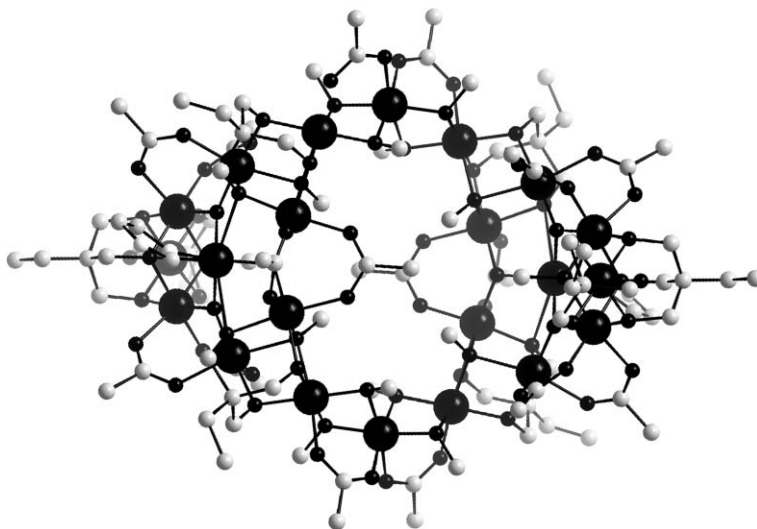


**Fig. 13** A representation of the structure of  $[\text{Mn}_{26}\text{O}_{17}(\text{OH})_8(\text{OMe})_4\text{F}_{10}(\text{L}^{29})_{22}(\text{MeOH})_{14}(\text{H}_2\text{O})_2]$ . The Mn centres are shown as large black spheres.

thereby demonstrating the utility of  $\text{MnF}_3$  as a new synthon in manganese cluster chemistry (Fig. 13).<sup>32</sup>

The synthesis and magnetic properties of three isostructural  $\text{Mn}_{16}$  clusters  $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{O}_2\text{CCH}_2\text{Ph})_{16}(\text{MeOH})_6]$ ,  $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{O}_2\text{CCH}_2\text{Cl})_{16}(\text{MeOH})_6]$ , and  $[\text{Mn}_{16}\text{O}_{16}(\text{OMe})_6(\text{O}_2\text{CCH}_2\text{Br})_{16}(\text{MeOH})_6]$  have been reported.<sup>33</sup> The complexes were prepared by a reductive aggregation reaction involving phenylacetic acid, chloroacetic acid or bromoacetic acid, and  $\text{N}^{\text{t}}\text{Bu}_4\text{MnO}_4$  in MeOH. The preparation and physical characterization of a novel SMM  $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{12}(\text{L}^{30})_4]$  ( $\text{HL}^{30}$  = diphenyl phosphate) with no coordinating water molecules has been reported.<sup>34</sup> Measurements and analyses of magnetization hysteresis and ac magnetic susceptibility indicated that the complex is a SMM with quantum tunnelling behaviour, the ground state of which was tentatively assigned to  $S = 10$  with  $g = 1.78$  and  $D \sim 0.60$  K. Furthermore, the site-specific ligation of anthracene-1,8-dicarboxylates to an  $\{\text{Mn}_{12}\}$  core has also been revealed as a route to the controlled functionalisation of single molecule magnets.<sup>35</sup> Mixed complexes of Re(II) and Mn(II) with a cube-like architecture have also been found to display SMM-like behaviour.<sup>36</sup>

The synthesis and magnetic properties of  $[\text{Mn}_{22}\text{O}_6(\text{OMe})_{14}(\text{O}_2\text{CMe})_{16}(\text{L}^{31})_8(\text{L}^{32})_2]$  are reported.<sup>37</sup> This complex was prepared by treatment of  $[\text{Mn}_3\text{O}(\text{MeCO}_2)_6(\text{L}^{32})_3](\text{MeCO}_2)$  ( $\text{L}^{32}$  = imidazole) with 1,1,1-tris(hydroxymethyl)propane,  $\text{H}_3\text{L}^{31}$ , in MeOH. The molecule consists of a metallic core of 2 Mn(IV), 18 Mn(III), and 2 Mn(II) ions, linked by a combination of 6  $\mu_3$ -bridging  $\text{O}^{2-}$  ions, 14  $\mu_3$ - and  $\mu_2$ -bridging  $\text{MeO}^-$  ions, 16  $\mu$ - $\text{MeCO}_2^-$  ligands, and 8  $(\text{L}^{31})^{3-}$  ligands—which use their alkoxide arms to bridge in a variety of ways (Fig. 14). The metal–oxygen core is best described as a wheel made from  $[\text{Mn}_3\text{O}_4]$  partial cubes and  $[\text{Mn}_3\text{O}]$  triangles. Magnetic investigations reveal behaviour consistent with that expected from a SMM,

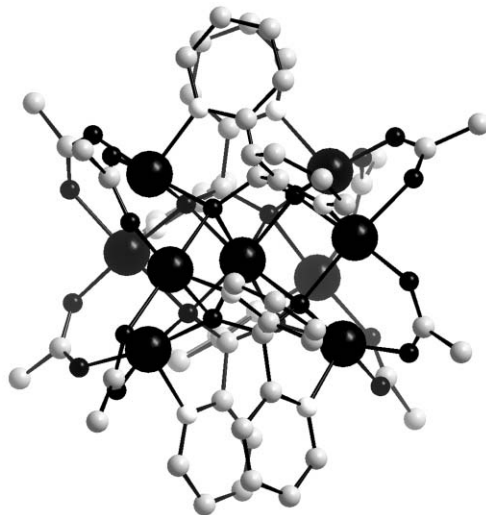


**Fig. 14** The structure of  $[\text{Mn}_{22}\text{O}_6(\text{OMe})_{14}(\text{O}_2\text{CMe})_{16}(\text{L}^{31})_8(\text{L}^{32})_2]$ . The Mn atoms are shown as large black spheres.

with a blocking temperature of approximately 1.3 K. The use of  $\{\text{Mn}_3\text{O}\}$  core units with different ligands is proving to be an exceptional route to new polynuclear Mn-based clusters.<sup>38</sup> Further, the reaction of the mixed valency metal triangles  $[\text{Mn}_3\text{O}(\text{O}_2\text{CR})_6(\text{py})_3]$  ( $\text{R} = \text{CH}_3, \text{Ph}, \text{}^t\text{Bu}$ ) with tripodal ligands produces a family of rod-like manganese complexes whose structures are all derived from a series of edge sharing triangles.<sup>39</sup> A carboxylate triangle consisting of three Mn(II) centres has also been synthesised from Mn(II) carbonate and pivalic acid.<sup>40</sup>

A new  $\{\text{Mn}_{25}\}$  SMM, with a record value of  $S = 51/2$  for a molecular species, has been reported. It is mixed valence with 6 Mn(II), 18 Mn(III) and 1 Mn(IV) centre. It also has an unusual five layer structure.<sup>41</sup> By extending from pure Mn to a new family of mixed  $\text{Mn}^{3+}\text{-Ln}^{3+}$  polynuclear SMMs comprising a  $[\text{Mn}_{11}\text{Ln}_4]^{45+}$  core, all but the Eu complex display the frequency-dependent, out-of-phase ac susceptibility signals suggestive of SMMs.<sup>42</sup> In similar work, a mixed  $\{\text{Dy}_6\text{Mn}_6\}$  cluster has been discovered that also displays SMM-like properties.<sup>43</sup> Also, a tetranuclear, oxo-bridged manganese cluster, a dimer-of-dimers ( $\text{Mn}(\text{II})_2, \text{Mn}(\text{IV})_2$ ), has been examined which is relevant to the photo-system II water oxidase active site. As the cluster is able to undergo structural rearrangements in solution, this raises questions about “shape-shifting” for the PSII  $\{\text{Mn}_4\}$  cluster.<sup>44</sup> A high spin molecular square comprising of square-pyramidal  $\text{Co}^{2+}$  and tetrahedral  $\text{Mn}^{2+}$  corners and exhibiting an overall  $S = 4$  ground state has been crystallized and its magnetic properties investigated.<sup>45</sup>

A novel supramolecular assembly containing Fe(III) centres coordinated to an oxo- and oxalate ligand forms a supramolecular, three-dimensional network that exhibits magnetic ordering at 70 K due to a weak spin canting.<sup>46</sup> The first member of a new class of Fe(II)-based SMMs,  $[\text{Fe}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8\{(2\text{-py})_2\text{CO}_2\}_4]$  (where  $[(2\text{-py})_2\text{CO}_2]^{2-}$  is the doubly-deprotonated gem-diol form of di-2-pyridyl ketone,  $\text{L}^{33}$ ), obtained by a rational synthetic route, has recently been reported (Fig. 15). Iron SMMs are of considerable interest, because the nuclear spin of the transition metal



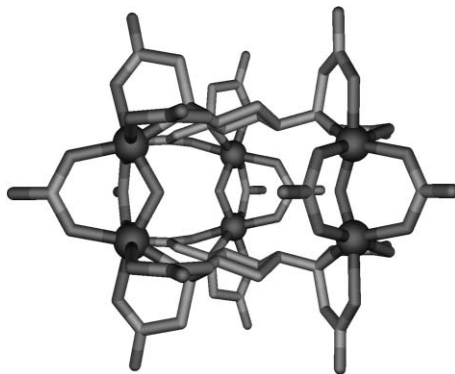
**Fig. 15** The structure of  $[\text{Fe}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8\{(2\text{-py})_2\text{CO}_2\}_4]$ . The Fe atoms are shown as large black spheres.

in a polynuclear SMM affects the rate of QTM (Mn has a nuclear spin of  $I = 5/2$ , whereas  $^{56}\text{Fe}$  has  $I = 0$ ). Moreover, Fe(II) centres are known to exhibit moderate-to-large single ion anisotropy in high spin ferrous complexes.<sup>47</sup> A range of tetranuclear Ni(II) complexes incorporating azide have also been discovered, in which the azide adopts an unprecedented central  $\mu_4$ -1,1,3,3-azide coordination mode.<sup>48</sup> Furthermore, a novel high spin heterometallic  $\text{Ni}_{12}\text{K}_4$  cluster incorporating azide ligands has recently been synthesised.<sup>49</sup> Reaction of di-2-pyridyl ketone,  $\text{L}^{33}$ , with nickel acetate and azide, in the presence of potassium *tert*-butylate as a catalytic base, generates the title compound, which contains the largest known  $[\text{Ni}(\mu\text{-}1,1\text{-N}_3)]_6$  circles in the discrete, ferromagnetically-coupled,  $\text{M}(\text{II})$ -azide cluster family, and shows an unprecedented *in situ* cyanomethylation of ketone.

The first all-cyanide  $[\text{Fe}_4\text{S}_4(\text{CN})_4]^{3-}$  cluster, which resembles the protein  $\text{Fe}_4\text{S}_4$  active sites both geometrically and spectroscopically, has been synthesised. Its 2-/3- and 3-/4- redox potentials of  $-0.4$  and  $-1.38$  V vs.  $\text{Ag}/\text{AgCl}$  are the least negative such potentials among all of the synthetic analogues of the  $\text{Fe}_4\text{S}_4$  protein active sites.<sup>50</sup> Heterometallic Ni/Fe/S and Cu/Fe/S clusters have also been synthesised with a pentlandite-like  $\text{M}_8\text{S}_6$  core.<sup>51</sup>

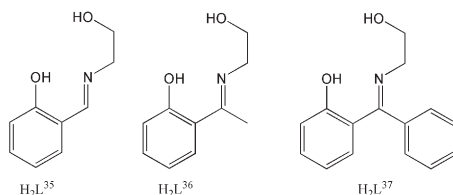
Complexation of the highly branched, pentadecadentate chelating ligand *cis*-1,3,5-cyclohexanetriamine-*N,N,N',N',N'',N''*-hexaacetic acid,  $\text{H}_6\text{L}^{34}$ , with Fe(III) and sodium cations in the presence of carbonate anions, leads to the formation of a  $\{\text{Fe}_6(\text{L}^{34})_2\}$  cluster comprising an  $\{\text{Fe}_6\}$  cage linked by 12 exo-coordinated sodium cations in an extended 3-D array (Fig. 16).<sup>52</sup>

Nine members of a new family of polynuclear ferric complexes have been synthesized and characterized. The reaction of  $\text{Fe}(\text{O}_2\text{CMe})_2$  with polydentate Schiff base proligands  $\text{H}_2\text{L}^{35-37}$ , derived from salicylidene-2-ethanolamine, followed in some cases by reaction with carboxylic acids, has afforded new complexes of general formula  $[\text{Fe}_2(\text{pic})_2(\text{L}^{35-37})_2]$  (where pic is the anion of 2-picolinic acid),  $[\text{Fe}_3(\text{O}_2\text{CMe})_3(\text{L}^{35-37})_3]$ ,  $[\text{Fe}_4(\text{OR})_2(\text{O}_2\text{CMe})_2(\text{L}^{35-37})_4]$  and  $[\text{Fe}_5\text{O}(\text{OH})(\text{O}_2\text{CR})_4(\text{L}^{35-37})_4]$ .<sup>53</sup> The



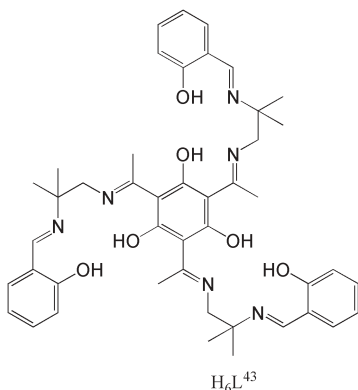
**Fig. 16** The structure of  $[\text{Fe}_6(\text{O})_3(\text{CO}_3)_6(\text{L}^{34})_2]^{12-}$  with the ligand backbone shown as sticks and the Fe atoms are shown as spheres.

reaction of anhydrous  $\text{FeCl}_3$  with 1*H*-benzotriazole-1-methanol in MeOH produces the pentanuclear complex  $[\text{Fe}_5\text{O}_2(\text{OME})_2(\text{L}^{38})_4(\text{HL}^{38})(\text{MeOH})_5\text{Cl}_5]$  ( $\text{L}^{38}$  = 1*H*-benzotriazole), containing a distorted tetrahedron of four Fe ions centred on a fifth. The central Fe is antiferromagnetically coupled to the peripheral Fe ions resulting in an  $S = 15/2$  spin ground state.<sup>54</sup> Density functional theory calculations and Monte Carlo simulations have been used to calculate the exchange interactions in the Fe(III) cluster  $[\text{Fe}_{14}(\text{L}^{38})_6\text{O}_6(\text{OME})_{18}\text{Cl}_6]$ , impossible to determine by conventional methods. The results support a huge ground state spin, arising from competing antiferromagnetic interactions.<sup>55</sup>



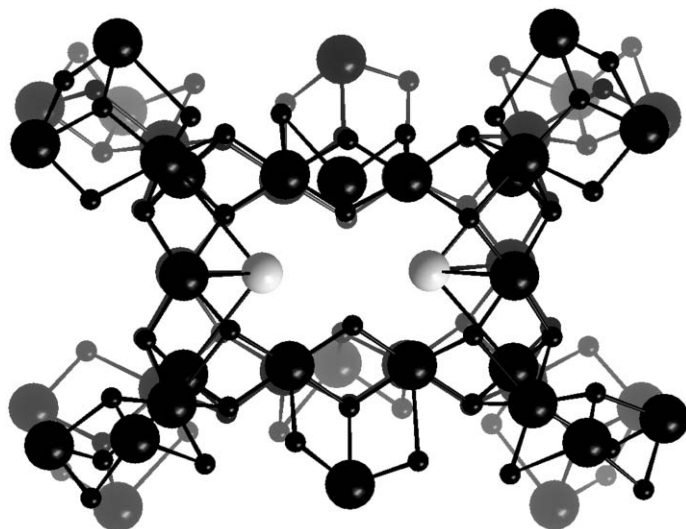
A supramolecular Fe metal–ligand assembly  $[\text{Fe}_4(\text{L}^{39})_6]^{12-}$  ( $\text{L}^{39}$  = 1,5-bis(2,3-dihydroxybenzamido)naphthalene), has been constructed that is capable of catalysing a unimolecular 3-aza-Cope rearrangement. This starts from the enammonium cation, a [3,3] sigmatropic rearrangement then leads to an iminium cation, which then hydrolyses to the aldehyde. Simply by inclusion into a size- and shape-constrained reaction space, these rearrangements are accelerated by up to three orders of magnitude compared to their background rates. Furthermore, the chemical properties of the reacting system provide an effective means of preventing product inhibition, which facilitates catalyst turnover.<sup>56</sup> By changing Fe to Ga to give  $[\text{Ga}_4(\text{L}^{39})_6]^{12-}$ , the host–guest chemistry of the tetrahedral capsule complex has been investigated. The capsule is soluble in water and other highly polar solvents, but contains a hydrophobic cavity of approximately 300–350 Å<sup>3</sup> that can encapsulate a variety of monocationic species. Furthermore, enantioselective guest binding and dynamic resolution of cationic ruthenium complexes has been observed.<sup>57</sup> The hexadentate and ditopic ligand 2,5-bis([2,2']bipyridin-6-yl)pyrazine,  $\text{L}^{40}$ , yields a

chiral, tetrameric, square shaped, self-assembled species upon complexation with Fe(II) ions. The racemate of this complex was resolved with antimonyl tartrate as the chiral auxiliary. The enantiomeric purity was determined by NMR spectroscopy using a chiral, diamagnetic shift reagent, and by circular dichroism. When a “chiralised” version of the ligand was used instead, the corresponding iron complex was obtained in a diastereomerically pure form.<sup>58</sup>



The reaction of  $\text{Cu}(\text{ClO}_4)_2$  and *N*-propylamine,  $\text{L}^{41}$ , in methanol gives two high nuclearity products with well-defined compositions. At amine concentrations greater than seven equivalents compared to the copper ion concentration, the system fixes carbon dioxide from the air to form the one-dimensional, carbamate-bridged coordination polymer  $\{[\text{Cu}(\mu_2\text{-O}, \text{O}'\text{-O}_2\text{CNH}(\text{CH}_2)_2\text{CH}_3)(\text{NH}_2(\text{CH}_2)_2\text{CH}_3)_3](\text{ClO}_4)\}_n$ . Interestingly, lower relative amine concentrations lead to the self-assembly of an octanuclear copper–amine–hydroxide cluster  $[\text{Cu}_8(\text{OH})_{10}(\text{NH}_2(\text{CH}_2)_2\text{CH}_3)_{12}]^{6+}$ . Magnetic susceptibility studies indicate very weak antiferromagnetic coupling for the polymer, whereas the octanuclear cluster displays a slightly stronger net antiferromagnetic coupling, despite the presence of a number of  $\text{Cu}-\text{O}(\text{H})-\text{Cu}$  bridges that would normally be expected to yield ferromagnetic coupling.<sup>59</sup> A range of coordination clusters of Cu(II) have been found utilising the ligand  $\text{H}_3\text{L}^{42}$ , 1,3-bis(3-oxo-3-phenylpropionyl)-2-hydroxy-5-methylbenzene. These clusters show various nuclearities from  $\{\text{Cu}_2\}$  to  $\{\text{Cu}_8\}$ , and have been magnetically characterised.<sup>60</sup> The trinuclear Cu(II) complex  $[(\text{L}^{43})\text{Cu}(\text{II})_3]$  has been synthesized and structurally characterized using the new triple-salen ligand,  $\text{H}_6\text{L}^{43}$ . The three Cu(II) ions are bridged in a *meta*-phenylene linkage by the phloroglucinol backbone of the ligand. This *meta*-phenylene bridging mode results in ferromagnetic couplings with a  $S_1 = 3/2$  spin ground state, that has been analyzed by means of EPR spectroscopy and DFT calculations. The EPR spectrum exhibits an unprecedented pattern of 10 hyperfine lines due to the coupling of three Cu(II) ions ( $I = 3/2$ ). The DFT calculations show an alteration in the sign of the spin densities of the central benzene ring, corroborating the spin polarization mechanism as the origin of the ferromagnetic coupling.<sup>61</sup> The syntheses, structural characterization, and magnetic behaviour of the three new polynuclear copper(II) complexes utilising the 1,3-bis(dimethylamino)-2-propanol ligand,  $\text{HL}^{44}$ , are reported:  $[\text{Cu}_4(\eta^2\text{-}\mu\text{-CH}_3\text{COO})_2(\mu\text{-OH})_2(\mu\text{-OH}_2)(\mu\text{-L}^{44})_2]^+$ ,  $[\text{Cu}_8(\text{NCO})_2(\eta^1\text{-}\mu\text{-NCO})_4(\mu\text{-OH})_2(\mu_3\text{-OH})_2(\mu\text{-OH}_2)_3(\mu\text{-L}^{44})_4]^+$  and  $[\text{Cu}_9(\eta^1\text{-}\mu\text{-NCO})_8(\mu_3\text{-OH})_4(\text{OH}_2)_2(\mu\text{-L}^{44})_4]^+$ . The magnetic behaviour of the three complexes shows strong





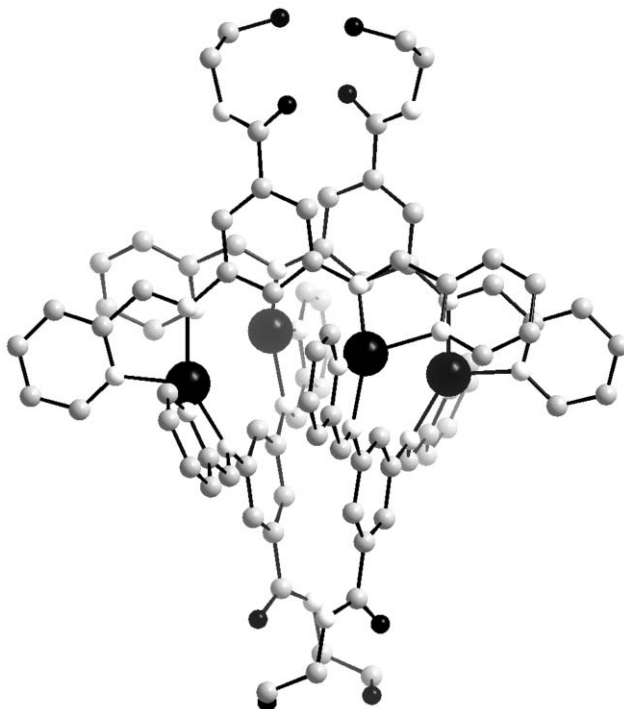
**Fig. 17** The structure of the  $\{\text{Cu}_{44}\}$  framework with the ligands and terminal oxo-ligands removed. The two  $(\mu_8\text{-Br})$  ions can be seen in the centre of the cavity. The Cu atoms are shown as large black spheres and the Br atoms as grey spheres.

antiferromagnetic coupling in all three cases.<sup>62</sup> The reaction of copper(I) iodide with tri-*meta*-tolylphosphine,  $\text{L}^{45}$ , in acetonitrile yielded the cluster  $[\text{Cu}_6(\mu_2\text{-I})(\mu_3\text{-I})_4(\mu_4\text{-I})(\text{L}^{45})_4(\text{CH}_3\text{CN})_2]$  with a bicapped, adamantoid geometry. In this compound, four Cu atoms are coordinated to four terminally bonded  $\text{L}^{45}$  ligands, two Cu atoms are bonded to two  $\text{CH}_3\text{CN}$  ligands, and the iodide ligands have  $\mu_2\text{-I}$ ,  $\mu_3\text{-I}$ , and  $\mu_4\text{-I}$  bonding modes. This compound has four  $\text{CuI}_3\text{P}$  and two  $\text{CuI}_3\text{N}$  cores, and the geometry around each Cu centre is distorted tetrahedral.<sup>63</sup>

Reaction of Cu(II) and aminopolycarboxylate nitrilotripropionic acid,  $\text{H}_3\text{L}^{46}$ , in water leads to the formation of  $[\text{Cu}_{44}(\mu_8\text{-Br})_2(\mu_3\text{-OH})_{36}(\mu\text{-OH})_4(\text{L}^{46})_{12}\text{Br}_8(\text{OH}_2)_{28}]^{2+}$  (Fig. 17). The  $\{\text{Cu}_{44}\}$  aggregates have a central inorganic core corresponding to  $[\text{Cu}_{24}(\mu_8\text{-Br})_2(\mu_3\text{-OH})_{24}(\mu\text{-OH})_8]^{14+}$ , anchored on two bromide anions; the core itself being encased in a shell of  $\text{Cu}^{2+}$ /ligand units. The aggregates pack into a distorted tetragonal array with a very open structure and containing large amounts of water of crystallization. The magnetic properties have been studied and, while complicated by the presence of low lying excited states, indicate that the individual clusters have non-zero spin ground states.<sup>64</sup>

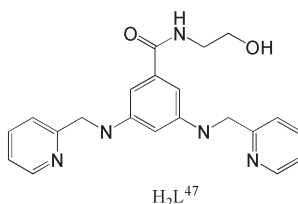
Addition of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  to aqueous solutions of Cu(II) in excess carbonate, promotes the assembly of a new highly charged carbonato-copper(II) anion,  $[\text{Cu}_4(\text{OH})(\text{CO}_3)_8]^{9-}$ , which contains an unusual  $\mu_4$ -hydroxo-bridged square  $\{\text{Cu}_4\}$  arrangement, stabilised in the crystal by *ca.* 40 hydrogen bonds ( $<3 \text{ \AA}$ ) to hexammine cations.<sup>65</sup> A  $[2 + 2]$  copper(I) grid has been prepared using  $\text{H}_2\text{L}^{47}$ , and possesses two novel features. Firstly the geometry of the grid structure is atypical, not being readily predictable from the “self-assembly instructions” encoded within the components. Secondly the ligands of grids generally cross at perpendicular junctions, which they cannot do in the present structure without distortion (Fig. 18).<sup>66</sup> Programmed, single step self-assembly of a  $[2 \times 2]$  grid architecture,



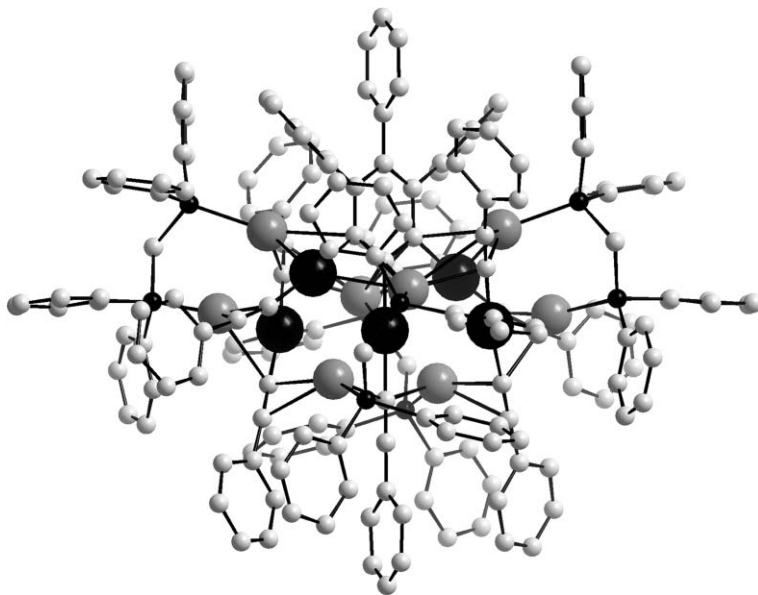


**Fig. 18** The structure of the  $[\text{Cu}_4(\text{L}^{47})_2]^{4+}$  [2+2] grid complex. The Cu atoms are shown by the large black spheres.

built on metallic centres of different coordination geometries, has also been achieved.<sup>67</sup> In this respect ‘self’ selection of complexes from a dynamic combinatorial library is being extended to a variety of systems.<sup>68</sup>



A tetranuclear Cu(II) cluster showing square planar geometry, formed with an aspartate bridging ligand,  $\text{L}^{48}$ , has been synthesized with the composition  $[\text{Cu}_4(\text{L}^{48})_2(\text{bpy})_4(\text{H}_2\text{O})_3]^{4+}$ . The global magnetic coupling is ferromagnetic, but theoretical DFT/B3LYP calculations are necessary to assign which Cu–L–Cu side is ferro- or antiferromagnetically coupled.<sup>69</sup> A triangular  $\{\text{Cu}(\text{II})_3\text{Cl}\}$  cluster, incorporating a chloro ligand in an unprecedented trigonal planar coordination mode, has been synthesised in the form of  $[\text{Cl}(\text{CuCl}_2\text{L}^{49}\text{H})_3]\text{X}_2$  ( $\text{L}^{49} = \text{cis,trans-1,3,5-triamino-cyclohexane}$ ,  $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ ). The cluster units are assembled into a 3-D array by the combination of coordinative and hydrogen bonded interactions, which results in magnetically isolated 1-D chains exhibiting a combination of spin frustration and spin-chain behaviour.<sup>70</sup> Octanuclear and nonanuclear supramolecular

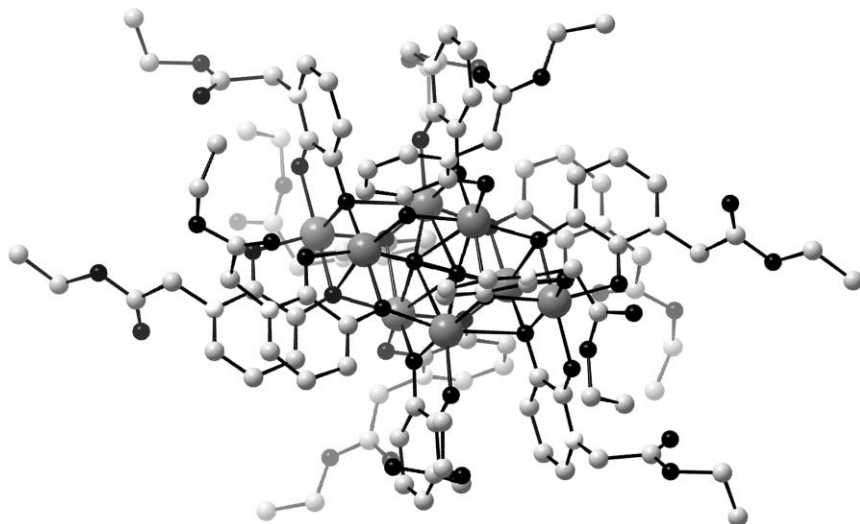


**Fig. 19** The structure of the luminescent heteronuclear  $\{\text{Au(I)}_5\text{Ag(I)}_8\}$  cluster complex. The Au and Ag atoms are shown as large black and large grey spheres respectively.

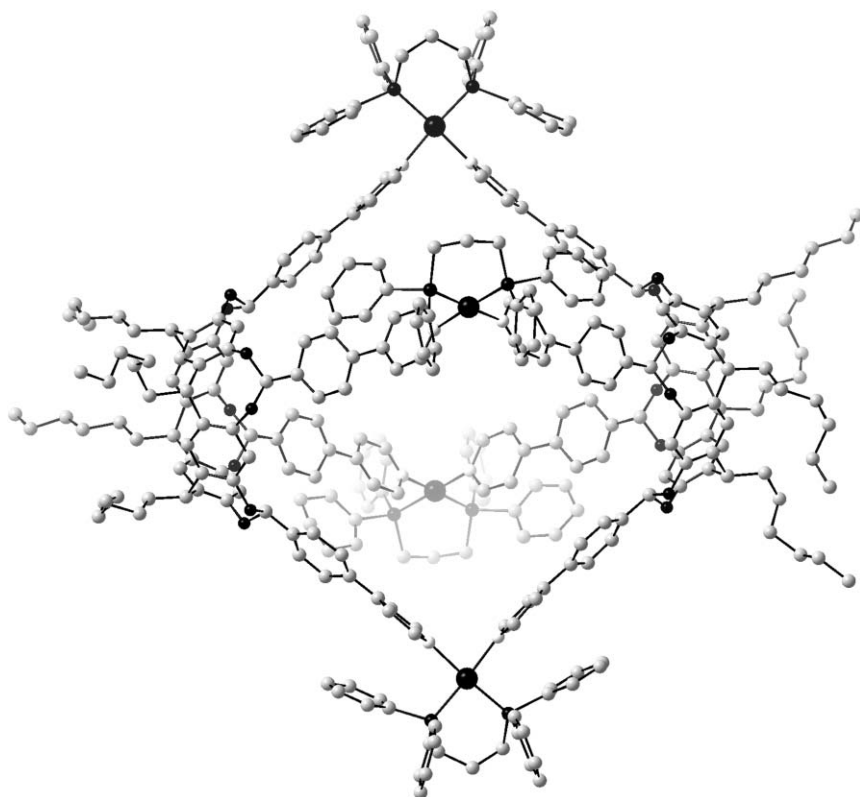
copper(II) complexes with linear “tritopic” ligands have been synthesised, their magnetic properties studied,<sup>71</sup> and utilised in the formation of an unusual dodecanuclear  $[\text{Co(II)}_6\text{Co(III)}_6]$  cluster.<sup>72</sup> Luminescent heteronuclear  $\{\text{Au(I)}_5\text{Ag(I)}_8\}$  cluster complexes were synthesised from polymeric silver arylacetylide,  $(\text{AgC}\equiv\text{CC}_6\text{H}_4\text{R-4})_n$ , with binuclear Au(I) components  $[\text{Au}_2(\mu\text{-L}^{50})_2(\text{MeCN})_2]^{2+}$  ( $\text{L}^{50}$  = bis(diphenylphosphino)methane).<sup>73</sup> Remarkably, the reaction allowed the isolation of Au(I)–Ag(I) heterometallic complexes  $[\text{Au}_5\text{Ag}_8(\mu\text{-L}^{50})_4\{1,2,3\text{-C}_6(\text{C}_6\text{H}_4\text{R-4})_3\}\text{-(C}\equiv\text{CC}_6\text{H}_4\text{R-4})_7\}]^{3+}$  ( $\text{R} = \text{H}, \text{CH}_3$  or  $^t\text{Bu}$ ) containing the unprecedented trianion  $\mu_5\text{-}\{1,2,3\text{-C}_6(\text{C}_6\text{H}_4\text{R-4})_3\}^{3-}$ , derived from cyclotrimerization of arylacetylide  $\text{C}\equiv\text{CC}_6\text{H}_4\text{R-4}$  (Fig. 19). A similar range of mixed Ag(I)–Cu(I) complexes have also been made using this approach.<sup>74</sup>

A rock-salt-like lattice structure consisting of monocationic and monoanionic Au(I)Ag(I)Cu(II) supramolecular cages of *d*-penicillamine has been discovered.<sup>75</sup> Reaction of  $\text{Zn}(\text{OAc})_2$  with pyrazine in refluxing ethanol gives the unusual heptanuclear complex  $\text{Zn}_7(\mu_4\text{-O})_2(\text{OAc})_{10}(\text{Pz})_2$  ( $\text{OAc}$  = acetate,  $\text{Pz}$  = pyrazine). Structural analysis reveals a central  $\{\text{Zn}_7\}$  core in which two pseudo-tetrahedral  $\{\text{Zn}_4\}$  units are joined at a common vertex.<sup>76</sup> The rational synthesis of an octahedral coordination capsule of composition  $[(\text{Pd}_3\text{HL}^{51})_8\{\mu\text{-(L}^{52})_{12}\}]^{16-}$  has been achieved, in which the triangular faces are covered by single ligands.<sup>77</sup> Complexes designed as potential MRI contrast agents have been synthesised based upon 1,2-hydroxypyridonate.<sup>78</sup> Ferromagnetic Ni(II)–Gd(III) interactions have been studied and explored in complexes with NiGd, NiGdNi and NiGdGdNi cores, supported by tripodal ligands.<sup>79</sup> Lanthanide heterometallic molecular squares containing  $\text{Ru}_2\text{–Ln}_2$  moieties and exhibiting sensitized near-infrared emission have also been synthesised.<sup>80</sup>



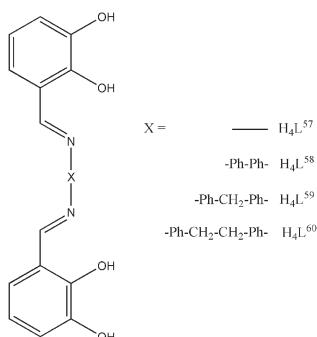


**Fig. 20** The structure of the  $[\text{Ni}_8(\text{L}^{53})_{12}(\text{O}_2)]^{2+}$  complex. The Ni atoms are shown by the large grey spheres.



**Fig. 21** The structure of  $[\text{Pd}(\text{L}^{55})_4(\text{L}^{56})_2]^{8+}$ . The Pd atoms are shown by the large black spheres.

catenation at both loops of the ‘figure-of-eight’ molecule.<sup>85</sup> A chiral [2]-catenane self-assembled from *meso*-macrocycles of Pd(II) has also been made,<sup>86</sup> the first time that this form of chiral [2]-catenane has been observed. The enantiomers of the [2]-catenane further self-assemble in the crystalline state, through secondary intermolecular Pd $\cdots$ X bonding, to form a racemic infinite supramolecular polymer of [2]-catenanes. A 3-D interlocked structure from a 2-D template has been assembled, showing that three-dimensional interlocked architectures can also be assembled from two-dimensional coordination templates by using steric and electronic restrictions to direct the synthesis in the third dimension. The resulting [2]-rotaxane is the first example of a mechanically-interlocked ligand that forms a four-coordinate, square-planar metal complex.<sup>87</sup> A general ligand system for assembling octahedral *meta*-rotaxane complexes of ions that prefer octahedral coordination, the commonest ligand geometry amongst transition metals, has been developed for rotaxanes.<sup>88</sup> A new Ru-containing metallamacrocycle has been obtained and fully characterized. Despite the relatively poor yield for the cyclization process involving the ruthenium centre (20%), this strategy led to the synthesis of two different kinds of [2]-catenane. The first example reported in this article is a bimetallic Cu(I)/Ru(II) catenane consisting of a purely organic ring, interlocked with the Ru(II)-incorporating metallacycle. This was selectively demetalated at the Cu(I) centre to lead to the free Ru(II)-containing catenane.<sup>89</sup>

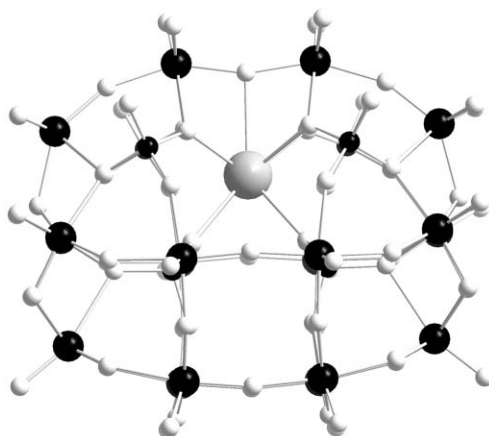


A series of bisimine-bridged dicatechol ligands, H<sub>4</sub>L<sup>57–60</sup>, have been designed to prepare triple-stranded dinuclear helicate-type complexes with a length of *ca.* 2 nm.<sup>90</sup> The helicates were formed by reaction with TiO(acac)<sub>2</sub> to give {Ti<sub>2</sub>L<sub>3</sub>} type complexes. Unsymmetrical ligands have also been used to form triple-stranded helicates with Ru(II).<sup>91</sup> Non-covalent intra-strand and inter-strand interactions have been used to prescribe helix formation within a metallosupramolecular system.<sup>92</sup> The effect of inter-strand and intra-strand interactions is explored in a metallosupramolecular system, in which the metal–ligand coordination requirements may be satisfied by more than one supramolecular architecture. Extended triple-stranded metallosupramolecular cylinders have also been successfully used to bind DNA.<sup>93</sup> Molecular chairs, zippers, zigzags and helical chains—four genuine supramolecular isomers—have all been formed, based on a pre-designed metal–organic building block [Cu(I)(L<sup>61</sup>)] (L<sup>61</sup> = 3,5-di-2-pyridyl-1,2,4-triazole).<sup>94</sup> Homochiral and heterochiral crystallizations of helical chiral polymer chains bridged by achiral poly-pyridyl ligands are dependent on the structures of the bridging ligands and independent of the solvent used, implying a possible strategy for the design of achiral crystals of helical chains using chiral bridging ligands.<sup>95</sup>

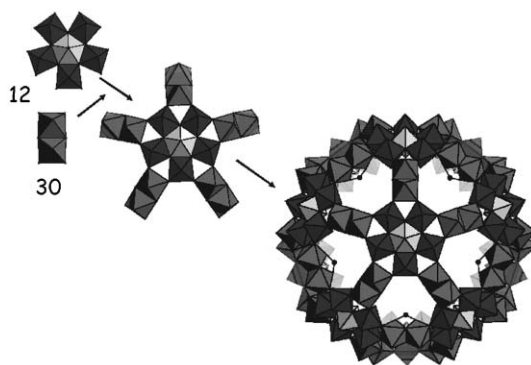
## 4. Polyoxometalates

The heteropoly-blue  $[\text{K} \subset \text{P}_6\text{Mo}_{18}\text{O}_{73}]^{11-}$ , with a basket-shaped skeleton, has been prepared using hydrothermal synthesis.<sup>96</sup> The cluster is a three electron reduced heteropoly-blue and shows reversible one electron redox properties. The framework is similar to the Wells–Dawson structural type, but this novel class of molecules includes six heteroatoms, rather than the two normally found for Dawson-type clusters (Fig. 22).

The highly charged nano-container capsule of type  $\{\text{pentagon}\}_{12}\{\text{linker}\}_{30} = \{(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}_2\text{O}_4(\text{SO}_4)\}_{30}$ , with 20 nanosized pores and channels, allows the entrance of cations like  $\text{Pr}^{3+}$ ; the latter are positioned at two different sites and have two different coordination shells, corresponding to a coordination chemistry under confined conditions. A fascinating aspect is that capsule-encapsulated water shells, fixed by hydrogen bonds, act formally as polydentate ligands.<sup>97</sup> Such Keplerate clusters (Fig. 23) can also be described as ‘artificial cells’,



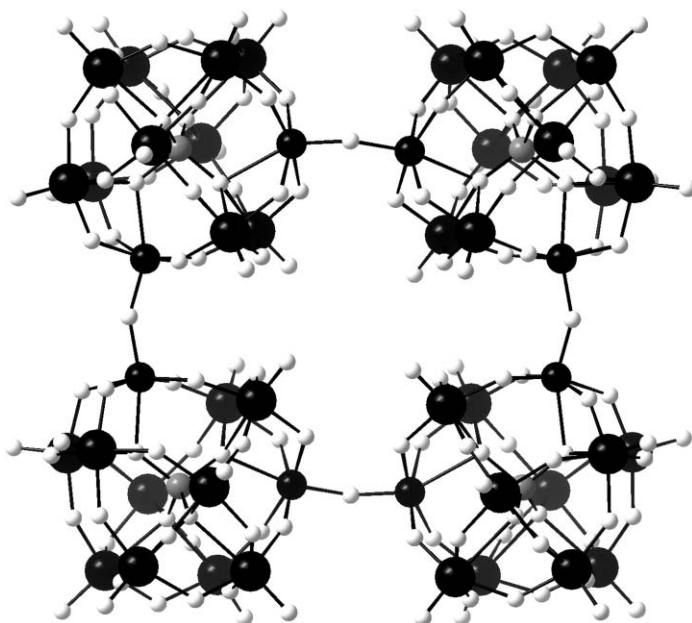
**Fig. 22** The structure of  $[\text{K} \subset \text{P}_6\text{Mo}_{18}\text{O}_{73}]^{11-}$ . The oxygen atoms are shown in white spheres, the potassium in grey and the molybdenum in black.



**Fig. 23** A schematic of the giant spherical ‘Keplerate’ cluster showing the composition based upon  $\{\text{pentagon}\}_{12}\{\text{linker}\}_{30}$ . The Mo-based metal centres are shown using a polyhedral representation.

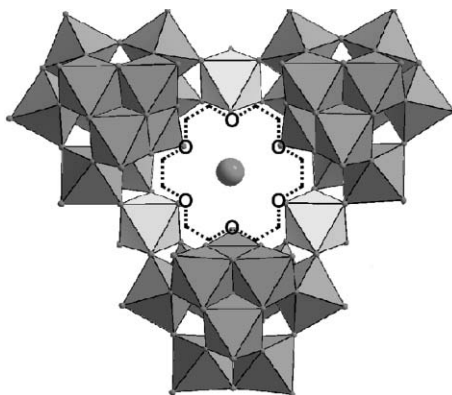
and this has been shown by the temperature-dependent, reversible  $\text{Li}^+$  ion uptake/release by such clusters.<sup>98</sup> Indeed, a temperature-dependent equilibrium process that involves the uptake/release of  $\text{Li}^+$  ions through the capsule pores and channels has also been shown to be present. The results have some relevance as a model for  $\text{Li}^+$  ion transport processes in clinical chemistry research.

A mesoporous, hydrogen bonded, organic–inorganic hybrid material has been built up from the assembly of isopolymolybdate  $[\text{Mo}_{36}\text{O}_{112}(\text{OH}_2)_{16}]^{8-}$  and  $\text{H}_2\text{bipy}^{2+}$ , and displayed large interconnected cavities and a reversible water sorption behaviour, while maintaining its striking crystal integrity.<sup>99</sup> A medium nuclearity, mixed-valence family of polyoxomolybdates based on  $[\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{10-}$ ,  $\{\text{Mo}_{16}\}$ , was synthesized using an approach that employed protonated hexamethylenetetramine ( $\text{HMTAH}^+$ ) as counter ion.<sup>100</sup> The  $\{\text{Mo}_{16}\}$  cluster anion exhibits significant nucleophilicity and traps electrophiles such as divalent transition metal ions, resulting in a family of isostructural compounds based on  $\{\text{Mo}_{16}\text{M}_2\}$ -type anions  $[\text{M}(\text{H}_2\text{O})_8\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{6-}$  ( $\text{M} = \text{Fe(II)}, \text{Mn(II)}, \text{Co(II)}$ ). Metallic conductivity down to 2 K in a polyoxometalate-containing radical salt of bis(ethylenedioxy) tetra-thiafulvalene (BEDO-TTF) has been observed.<sup>101</sup> The compound, formulated as  $[\text{BEDO-TTF}]_6\text{K}_2[\text{BW}_{12}\text{O}_{40}]$ , is formed by the polyoxometalate ion  $[\text{BW}_{12}\text{O}_{40}]^{5-}$  and BEDO-TTF. Structural control on a nanomolecular scale has been shown by the self-assembly of the polyoxotungstate wheel  $\{\text{W}_{40}\}^{24-}$ .<sup>102</sup> Here, interaction of solid  $\text{TiO}(\text{SO}_4)$  with  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  in the ratio 2 : 1 in an aqueous acidic medium (pH 2) resulted in the novel, tetrameric  $[\{\beta\text{-Ti}_2\text{SiW}_{10}\text{O}_{39}\}_4]^{24-}$  (Fig. 24). The polyanion is the first cyclic, tetrameric polyoxotungstate and is also the largest titanium-substituted tungstosilicate known to date.



**Fig. 24** A representation of the structure of  $[\{\beta\text{-Ti}_2\text{SiW}_{10}\text{O}_{39}\}_4]^{24-}$ . The oxygen atoms are shown as white spheres, the tungsten atoms as large black spheres, the titanium atoms as smaller black spheres and the silicon atoms as grey spheres.





**Fig. 25** A polyhedral plot of the  $[\text{KcW}_{36}]^{11-}$  cluster, with the W centres shown in polyhedra (the linking units in lighter grey) and the central potassium ion shown as a sphere. An 18-C-6 framework is superimposed on the central moiety to show the correspondence between the crown and the central oxygen framework in the cluster.

Strong ferromagnetic interactions have been seen in  $[\text{V}_8\text{O}_{14}(\text{H}_2\text{L}^{62})_2]$ , which yields an unprecedentedly large spin ground state for the vanadyl cluster.<sup>103</sup> The cluster is supported by the multiply-bridging ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol,  $\text{L}^{62}$ . The dimeric, pentacopper(II)-substituted tungstosilicate  $[\text{Cu}_5(\text{OH})_4(\text{H}_2\text{O})_2(\text{A-R-SiW}_9\text{O}_{33})_2]^{10-}$  has been synthesized in good yield using a one pot procedure by reaction of Cu(II) ions with the trilacunary precursor salt  $\text{K}_{10}[\text{A-R-SiW}_9\text{O}_{34}]$ . This polyanion represents the first polyoxotungstate substituted by 5 copper centres, and the central copper–hydrox–aqua fragment is completely unprecedented. In the course of the reaction, two  $[\text{A-R-SiW}_9\text{O}_{34}]^{10-}$  Keggin half units have fused in an asymmetrical fashion, resulting in the lacunary polyoxotungstate  $[\text{Si}_2\text{W}_{18}\text{O}_{66}]^{16-}$ . The vacancy in this species is stabilized by a magnetic cluster of five octahedrally-coordinated Cu(II) ions.

A high nuclearity “Celtic-Ring” isopolyoxotungstate,  $[\text{H}_{12}\text{W}_{36}\text{O}_{120}]^{12-}$ , has been discovered that captures trace potassium ions. It is prepared using a novel synthetic approach to the synthesis of cluster architectures by using ‘restraining’ or sterically demanding organo counter-cations to trap a  $\{\text{W}_{36}\}$ -based cluster.<sup>104</sup> This compound was isolated in the form  $(\text{TEAH})_9\text{Na}_2(\text{H}_2\text{O})_4\text{K}[\text{H}_{12}\text{W}_{36}\text{O}_{120}]$  (TEAH = protonated triethanolamine) includes the 3-fold symmetric cluster anion  $[\text{H}_{12}\text{W}_{36}\text{O}_{120}]^{12-}$  (Fig. 25).

A polyoxometalate containing the  $\{\text{Ni}_2\text{N}_3\}$  fragment has been found in a Ni(II)( $\mu$ -1,1-azido) complex, displaying ferromagnetic coupling and a large bridging angle.<sup>105</sup> The structural characterization and magnetic properties of complex  $\text{KRb}_5[(\text{PW}_{10}\text{O}_{37})\{\text{Ni}(\text{H}_2\text{O})_2(\mu\text{-N}_3)\}]$  constitute the first example of a fully-characterized azido polyoxometalate. Moreover, the topology of the  $\{\text{Ni}(\mu\text{-1,1-N}_3)\text{Ni}\}$  core is unprecedented, as no other corner sharing, azido-bridged Ni(II) complex has been obtained to date. It follows that the Ni–N–Ni angle is by far the largest observed in azido-ligand bridged Ni(II) compounds, a feature which should help the understanding of the relationships between structural parameters and the value of the magnetic exchange parameter  $J$  for  $\mu\text{-1,1-N}_3$  complexes.



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