DALTON
FULL PAPER

Supramolecular motifs: sextuple aryl embraces in crystalline $[M(2,2'\text{-bipy})_3]$ and related complexes†

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Tris(bidentate ligand)metal complexes such as $[M(bipy)_3]$ commonly associate in crystals as columns of complexes with collinear three-fold axes, in order that three heterocyclic rings of one complex can engage in six vertex-to-face interactions with three heterocyclic rings from the neighbour. This concerted supramolecular motif is called the sextuple aryl embrace (SAE), and is analogous to the sextuple phenyl embrace formed by XPh_3 and XPh_4 molecules. The three oxidation states of $[Ru(bipy)_3]^z$, $z = 0, 2+, 3+$, were found to crystallise with SAEs, as do most other $[M(bipy)_3]^z$ complexes with small symmetrical anions. Expansion of crystal lattices to accommodate anions was found not to disrupt the infinite columns of SAEs. A pair of tris(bidentate ligand)-metal complexes must have opposite chirality to participate in an SAE, and in this way the SAE differs from the otherwise similar homochiral helicate complexes. A small number of tris(tridentate ligand) complexes demonstrate a similar crystal supramolecular motif.

Advances in knowledge of supramolecular chemistry are organised around recurring supramolecular motifs, encompassing many molecular functionalities.[1–4] These motifs are recognised through analysis of crystal packing, and are deployed in crystal engineering.[5–7] We have previously described multiple phenyl embraces which occur between Ph_4P^+ ions and between Ph_3P ligands in the crystalline state.[8–11] The most common of these is the sextuple phenyl embrace (SPE), in which three Ph rings on one molecule are oriented between three Ph rings on the other molecule such that there is a supramolecular concert of six edge-to-face (**ef**) intermolecular phenyl–phenyl attractions. In addition to the SPE, two quadruple phenyl embraces which occur frequently are the OQPE (orthogonal quadruple phenyl embrace) and the PQPE (parallel quadruple phenyl embrace), named according to the orthogonal or parallel relationship between the relevant $C_{ipso}PC_{ipso}$ planes on each molecule.

The SPE is a consequence of the mutual conformation of three phenyl rings on a molecule. We questioned whether a similar conformation of aryl rings would occur around the three-fold axial faces of tris(bidentate ligand)metal complexes, such as $M(bipy)_3$,‡ by interrogation of the Cambridge Structural Database.[12,13] Fig. 1 shows that these ring conformations are indeed very similar, and that the bowl formed by the three aryl rings is slightly deeper for $M(bipy)_3$. Examination of the crystal structures of a variety of $[M(bipy)_3]^z$ complexes then revealed that these molecules do engage in embraces along the three-fold or quasi-three-fold axes of the molecules. We designate these as sextuple aryl embraces (SAE), using ‘aryl’ to encompass heteroaromatic substructures.

Sextuple Aryl Embraces formed by $[Ru(bipy)_3]^{0,2+,3+}$

Fig. 2 shows details of the SAE which occurs in crystalline $[Ru(bipy)_3]^0$ [TIWPEU] §,[14] in comparison with the SPE between two Ph_4P^+ ions.[8,9] The recent description[14] of the crystal structure of $[Ru(bipy)_3]^0$ noted the alignment of a pair of $[Ru(bipy)_3]^0$ molecules along a three-fold axis and the close approach of opposing pyridyl rings. Both three-fold ends of $[Ru(bipy)_3]^0$ can and do participate in sextuple aryl embraces, and the crystal structure is comprised of linear columns of molecules embracing this way along the three-fold axes: $-[Ru(bipy)_3]-SAE-[Ru(bipy)_3]-SAE-[Ru(bipy)_3]-$. The crystal lattice is trigonal, space group $P\bar{3}c1$, and there are two crystallographically distinct but similar molecules, generating two slightly different columns of SAE, as shown in Fig. 3. Geometrical details of these and other sextuple aryl embraces between $[M(bipy)_3]$ are presented below, but at this stage we introduce the characteristic distance between the two M atoms, which in $[Ru(bipy)_3]^0$ is 7.72 Å (= $c/2$) in both columns.

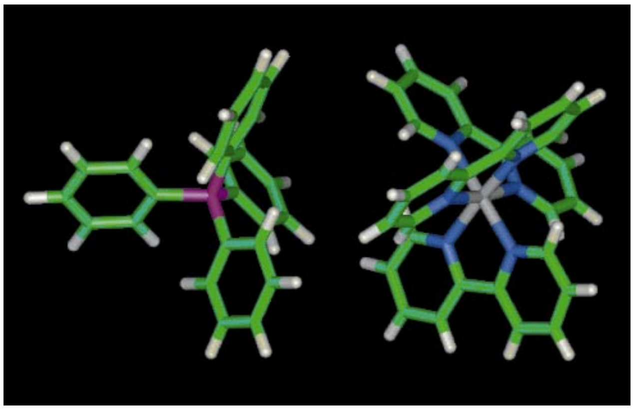

Fig. 1 Comparison of the quasi-three-fold array of phenyl rings for Ph_4X and the three-fold array of three pyridyl rings in $M(bipy)_3$: compare the three-fold arrays pointing to the right along the three-fold axis in each case. Note that the bowl formed by three ligands in $M(bipy)_3$ is deeper than that of Ph_4X or Ph_3X

In crystalline $[Ru(bipy)_3]^0$ there are also multiple aryl–aryl interactions between molecules in different SAE columns. Between pairs of molecules in different columns coloured aqua in Fig. 3 there are parallel quadruple aryl embraces, PQAE, analogous to the parallel quadruple phenyl embrace previously defined,[10] and shown in Fig. 4. There are edge-to-face (**ef**) interactions between pairs of molecules in the green and aqua columns of Fig. 3. Molecules on adjacent columns are offset by $c/4$ (erroneously stated as $c/2$ in the original paper[14]).

The significance of the SAE between $[M(bipy)_3]$ complexes is demonstrated by its occurrence in numerous other crystalline compounds, including the chemically famous oxidation states of ruthenium, $[Ru(bipy)_3]^{2+}$ and $[Ru(bipy)_3]^{3+}$. The crystal structure of $[Ru(bipy)_3][PF_6]_2$ [BPYRUF10] at room temper-

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† *Non-SI unit employed*: cal = 4.184 J.

‡ bipy = 2,2′-Bipyridine.

§ The reference codes for the crystal structures in the Cambridge Structural Database are provided in square brackets.

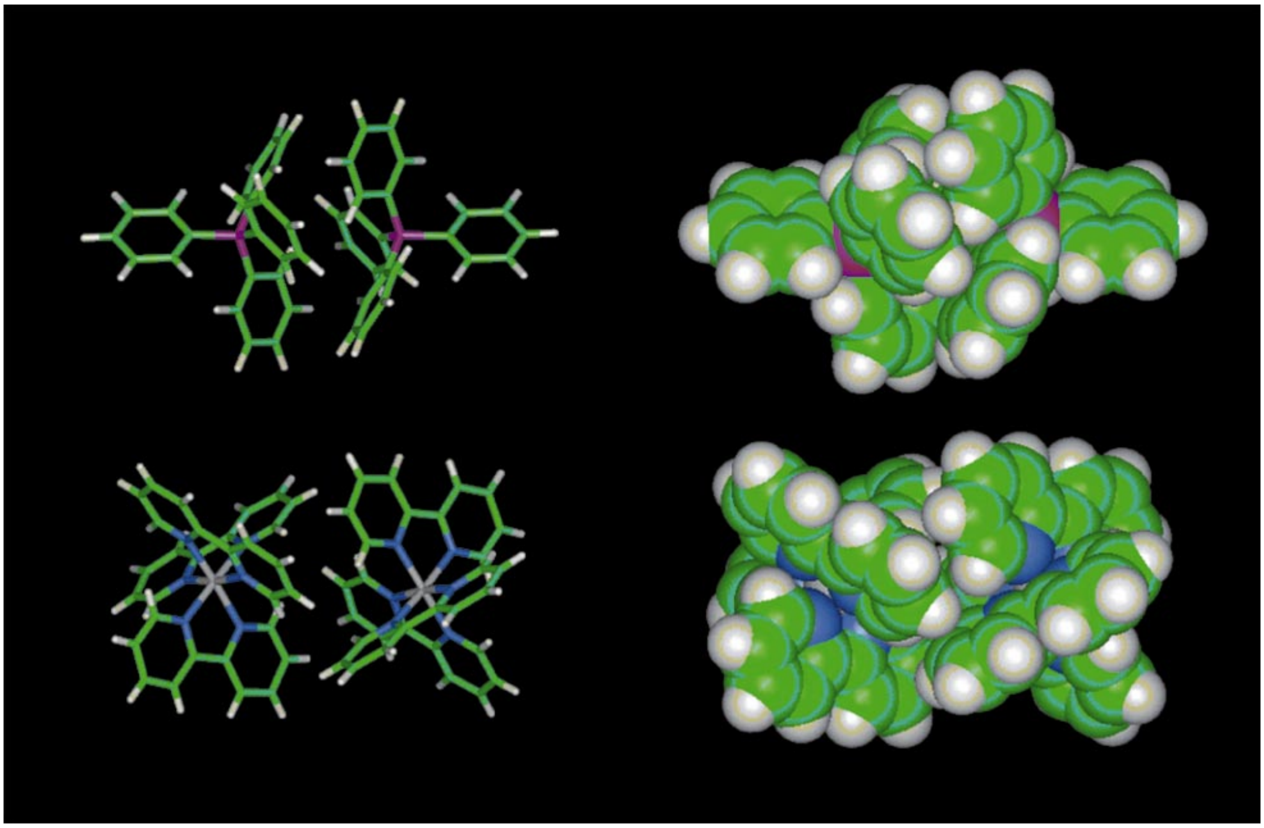


Fig. 2 Comparison of a typical sextuple phenyl embrace formed by two Ph_4P^+ ions (above) and the sextuple aryl embrace formed by two molecules of [Ru(bipy)$_3$] [TIWPEU] (below)

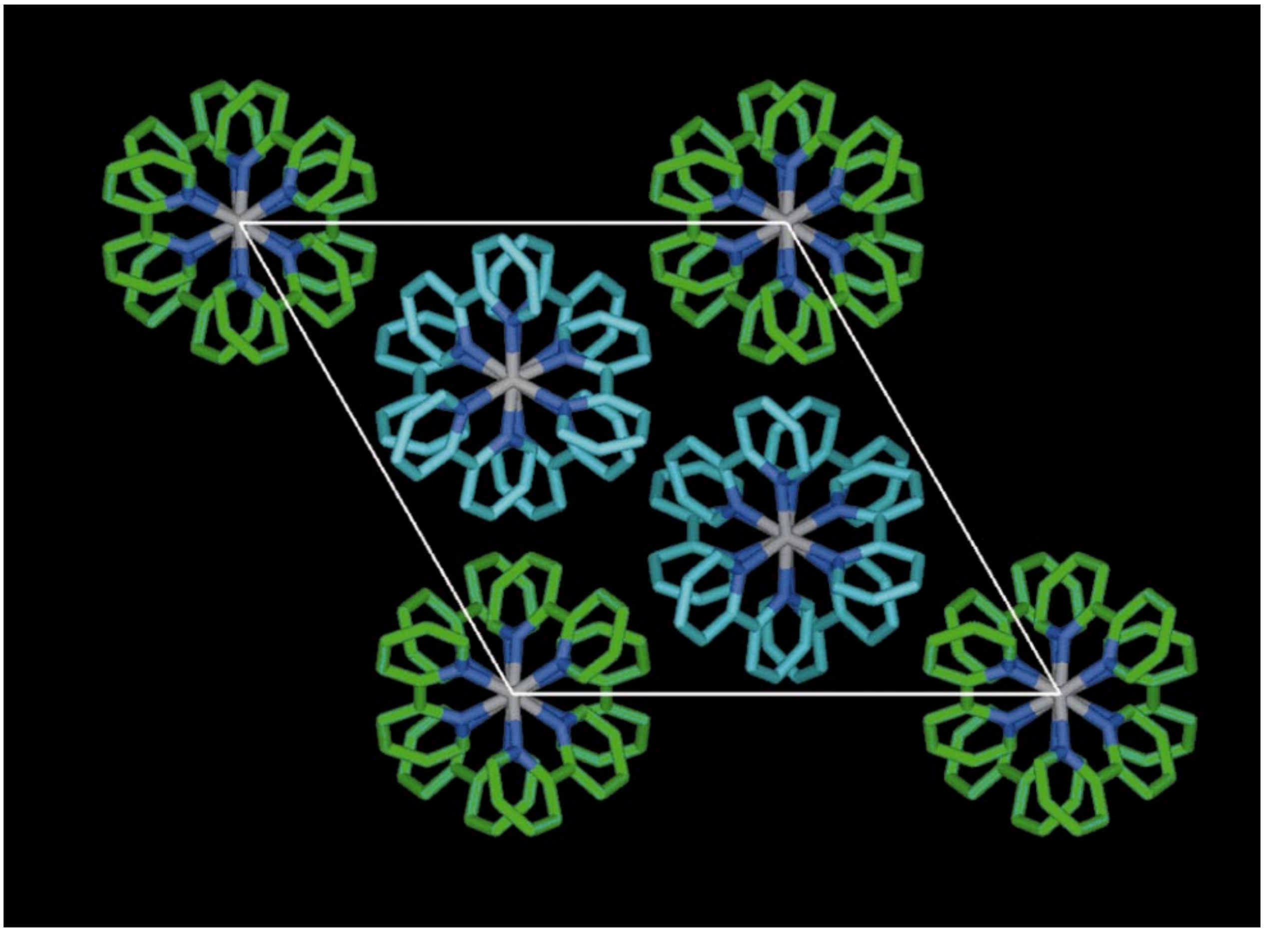


Fig. 3 The trigonal crystal lattice for $[Ru(bipy)_3]^0$ [TIWPEU], in space group $P\bar{3}c1$ with cell dimensions $a = b = 16.56$, $c = 15.44$, viewed along the columns of sextuple aryl embraces. The Ru atoms are silver, and H atoms are omitted. The two slightly different molecules and columns are colour-differentiated. The molecules in the column coloured green have local symmetry D_3, and are propagated by centres of inversion located at the centroids of the SAEs. The molecules in the aqua-coloured column have local symmetry C_3, are propagated along the column by the *c*-glide plane, and the SAEs have C_3 local symmetry

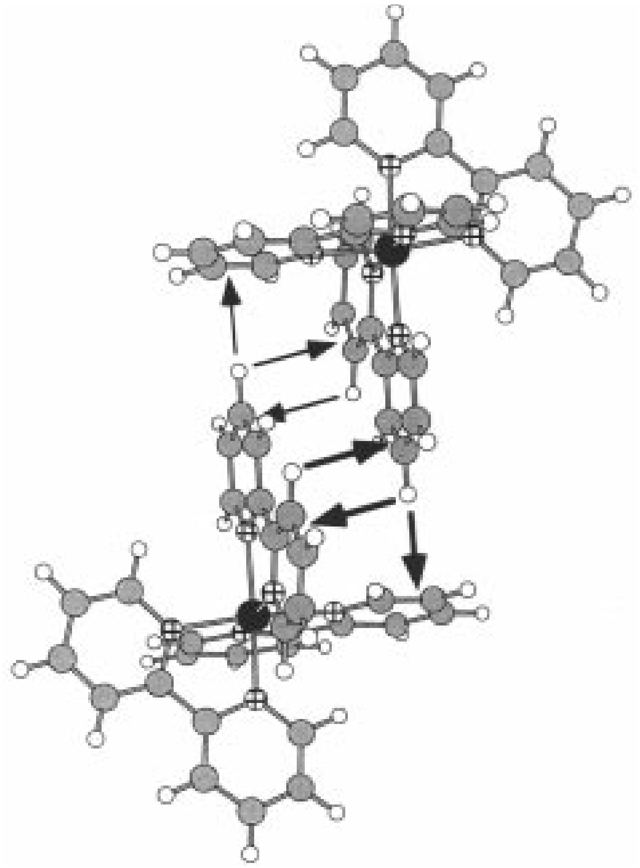


Fig. 4 The local vertex-to-face and offset face-to-face interactions between pyridyl groups comprising the parallel quadruple aryl embrace (PQAE) between columns in crystalline $[Ru(bipy)_3]^0$ [TIWPEU]. The most significant non-bonded H · · · C interactions are marked as arrows

ature is illustrated in Fig. 5. Again there are columns of complexes $[Ru(bipy)_3]^{2+}$ linked by SAE, but the columns have been separated slightly relative to those in $[Ru(bipy)_3]^0$ in order to accommodate the PF_6^- ions. The space group is the same as that of $[Ru(bipy)_3]^0$, but the positions of the columns of slightly different $[Ru(bipy)_3]^0$ are now occupied by the smaller PF_6^- ions, and the $a = b$ axes are reduced from 16.56 to 10.76 Å. The Ru · · · Ru distance in the SAE increases slightly to 8.2 Å. Even though the anions appear to occupy columns surrounding the cations, with anion–anion separations along the columns of $P \cdots P > 8$ Å, in fact the anions nestle between the cations, with specific cation–anion interactions. These are manifest as C–H · · · F interactions, with the shortest C · · · F distance being less than 3.2 Å. There are additional interactions between the columns of cations, as modified PQAEs in which the four rings involved are from one complete bipy ligand (on one metal centre) and two rings from different ligands (on the other metal centre) (see Fig. 6).

Crystalline $[Ru(bipy)_3][PF_6]_2$ undergoes a phase change at 190 K, and the crystal structure at 105 K [BPYRUF01] has lower symmetry (space group $P31c$) due to small shifts in positions of the anions and concomitant small shifts in the locations of the cations along the three-fold axes (see Fig. 7). The unit cell is slightly less than tripled in volume ($a = b = 18.34$, $c = 16.22$ Å) relative to the room-temperature polymorph. The SAEs are retained, but become inequivalent with three different Ru · · · Ru separations of 7.81, 8.11 and 8.41 Å. There is an increase in the number of C–H · · · F interactions between the cations and anions. The inter-column interactions (Fig. 6) noted for the high-temperature polymorph persist in the low-temperature modification.

Further oxidation to $[Ru(bipy)_3]^{3+}$ and incorporation of another anion in the lattice of crystalline $[Ru(bipy)_3][PF_6]_3$ [KUFDOE] does not disrupt the columns of $[Ru(bipy)_3]^{3+}$ in sextuple aryl embraces, as shown in Fig. 8. However, a

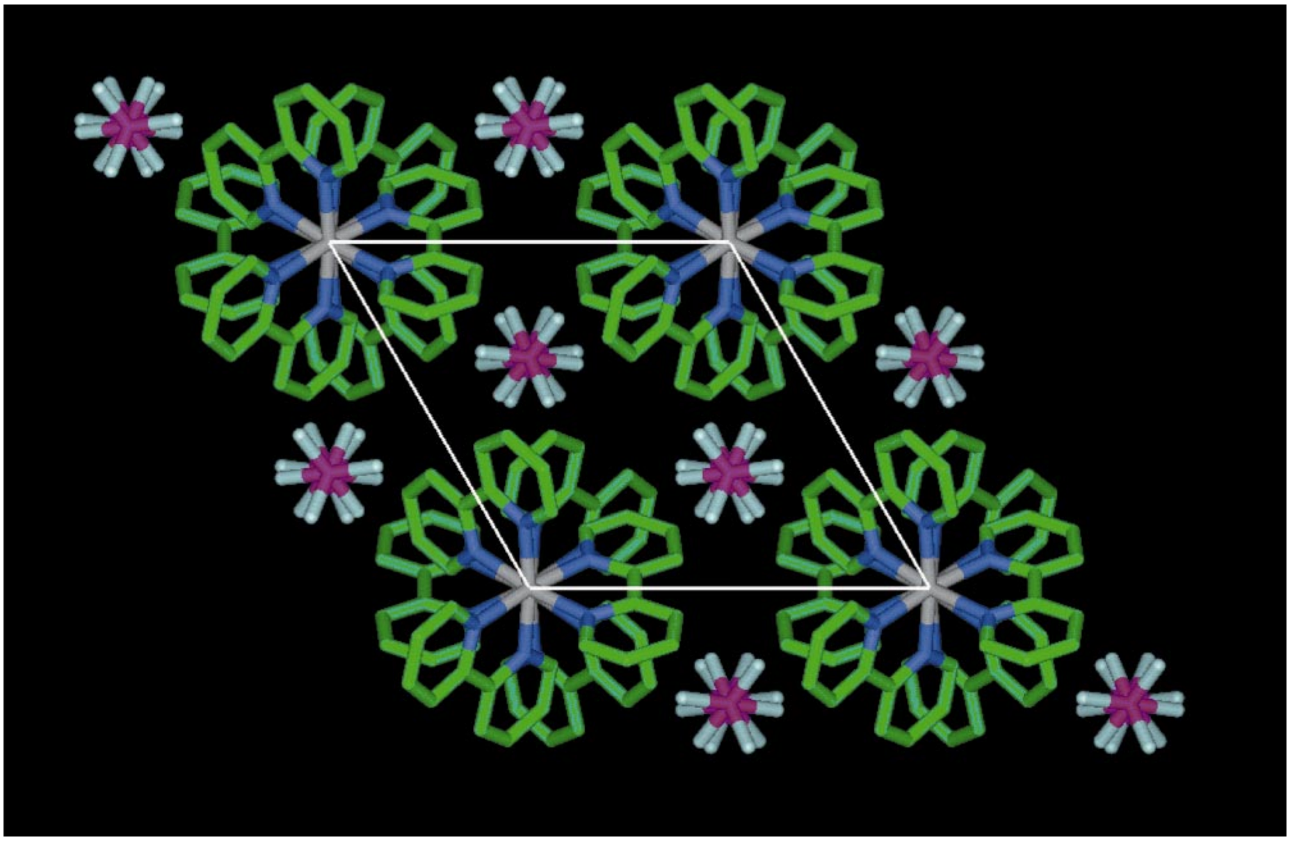


Fig. 5 The trigonal lattice of crystalline $[Ru(bipy)_3][PF_6]_2$ [BPYRUF10] at room temperature, viewed along the columns of $[Ru(bipy)_3]^{2+}$ cations connected by sextuple aryl embraces. Colours are as for Fig. 3, and with P pink, F white. The space group is $P\bar{3}c1$ and the cell dimensions $a = b = 10.76$, $c = 16.39$

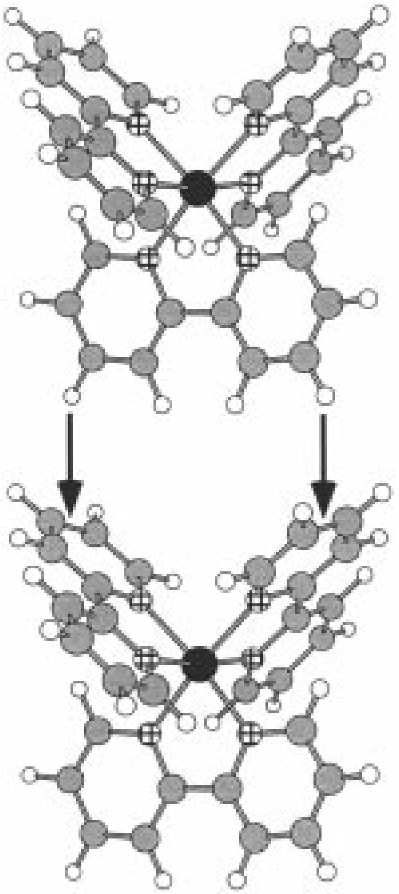
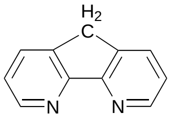


Fig. 6 The local vertex-to-face interactions between bipyridyl ligands in different columns of cations in crystalline $[Ru(bipy)_3][PF_6]_2$ at room temperature [BPYRUF10]. The most significant H···C interactions are marked

consequence of the additional anions in the lattice is that there is a larger number of C–H···F interactions between cations and anions, and fewer significant cation to cation CH···C interactions between columns: the Ru···Ru separation of cations along the columns increases to 9.96 Å.

Sextuple Aryl Embraces in other Crystalline Tris(bidentate ligand)metal Complexes

These crystal structures with columns of SAE are not restricted to these ruthenium compounds. The data in Table 1 show that $[V(bipy)_3]^0$ is isomorphous with $[Ru(bipy)_3]^0$; $[Os(bipy)_3][PF_6]_2$, $[Tc(bipy)_3][PF_6]_2$ and $[Re(bipy)_3][ReO_4]_2$ are isomorphous with $[Ru(bipy)_3][PF_6]_2$; and $[Cr(bipy)_3][PF_6]_3$ is isomorphous with $[Ru(bipy)_3][PF_6]_3$.¶ Variations in molecular structure do not change crystal structure. This point is reinforced by the crystal structure of $[Ru(bipy)_2(L^1)][PF_6]_2$ [COMVIJ] in which one of the bipyridyl ligands is replaced by 4,5-diazafluorene, L^1.



L^1

The crystal structure of the modified $[Ru(bipy)_3]^{2+}$ complex **1** (see Table 2) in which the donor N atom of one ligand is replaced by C is also isomorphous and isostructural with $[Ru(bipy)_3][PF_6]_2$ (room-temperature dimorph), with the location of the C atom being disordered over all N sites.

¶ Reports of structure analyses of $[Cr(bipy)_3][PF_6]_3$ and $[Rh(bipy)_3][PF_6]_3$ ([FERYEG] and [FERYIK], respectively) in space group $R32$ are considered to be incorrect, with a redetermination of the Cr structure [FERYEG01] indicating $R\bar{3}c$; it is therefore considered likely that $[Rh(bipy)_3][PF_6]_3$ is also isostructural with $[Ru(bipy)_3][PF_6]_3$.

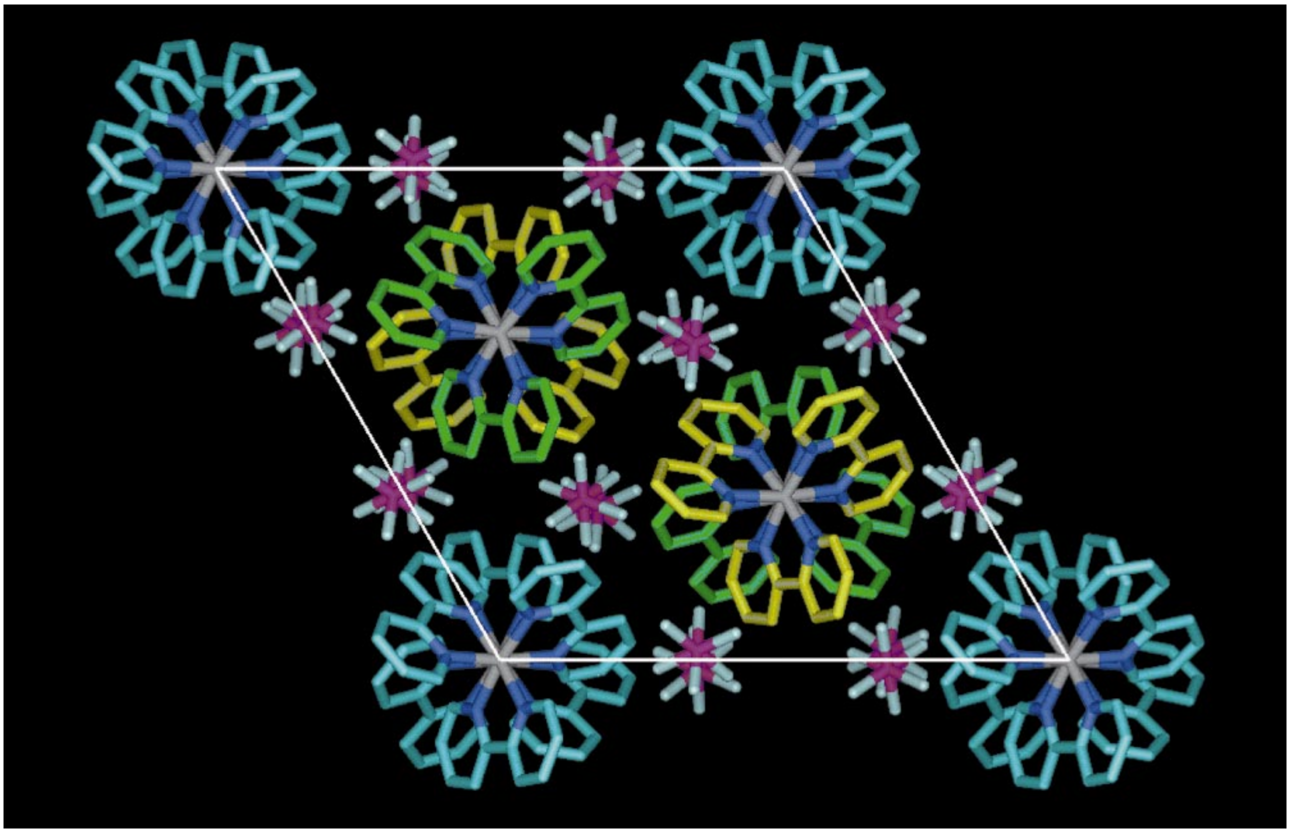


Fig. 7 Three-fold representation of the trigonal crystal structure of $[Ru(bipy)_3][PF_6]_2$ at 105 K [BPYRUF01]. The space group is $P31c$, and $a = b = 18.34$, $c = 16.22$ Å: colours as for Fig. 5. The anions are located at positions with no crystallographic symmetry, while the cations all have exact local symmetry C_3 (3) with the aqua cations having a Ru···Ru separation of 8.11 Å, while the green and yellow cations have Ru···Ru distances alternating between 7.81 and 8.41 Å

Table 1 Crystals containing $[M(bipy)_3]^z$ which occur as linear (or near linear) chains of molecules forming sextuple aryl embraces

Refcode	Compound[a]	Space group	Cell dimensions[b] *a*,*c* or *a*,*b*,*c*,β	M···M along the column/Å	M···M···M/°
TIWPEU	RuL_3	$P\bar{3}c1$	16.6, 15.4	7.72	180
DPYRDV	VL_3	$P\bar{3}c1$	16.9, 15.5	7.76	180
BPYRUF10	$[RuL_3][PF_6]_2$	$P\bar{3}c1$	10.8, 16.4	8.20	180
KAZXUE01	$[OsL_3][PF_6]_2$	$P\bar{3}c1$	10.8, 16.4	8.18	180
SUDZOG	$[TcL_3][PF_6]_2$	$P\bar{3}c1$	10.9, 16.3	8.15	180
FEZLOL	$[ReL_3][ReO_4]_2$	$P\bar{3}c1$	10.6, 16.4	8.22	180
BPYRUF01	$[RuL_3][PF_6]_2$	$P31c$	18.3, 16.2	8.11	180[c]
	(105 K)			8.41, 7.81	179.9[d]
FERYEG01	$[CrL_3][PF_6]_3$	$R\bar{3}c$	17.98, 19.96	9.98	180
KUFDOE	$[RuL_3][PF_6]_3$ (105 K)	$R\bar{3}c$	17.85, 19.92	9.96	180
ZAMGAV02	$[ZnL_3][ClO_4]_2$	$C2/c$	17.41, 10.90, 16.15, 91.22	8.10	171.6
HEGMIP01	$[RuL_3][ClO_4]_2$	$C2/c$	17.63, 10.75, 15.92, 90.76	7.97	173.6

[a] L = 2,2′-Bipyridyl. [b] *a*,*b*,*c* in Å, β in °. [c] For molecules coloured blue in Fig. 7. [d] For molecules coloured green and yellow in Fig. 7.

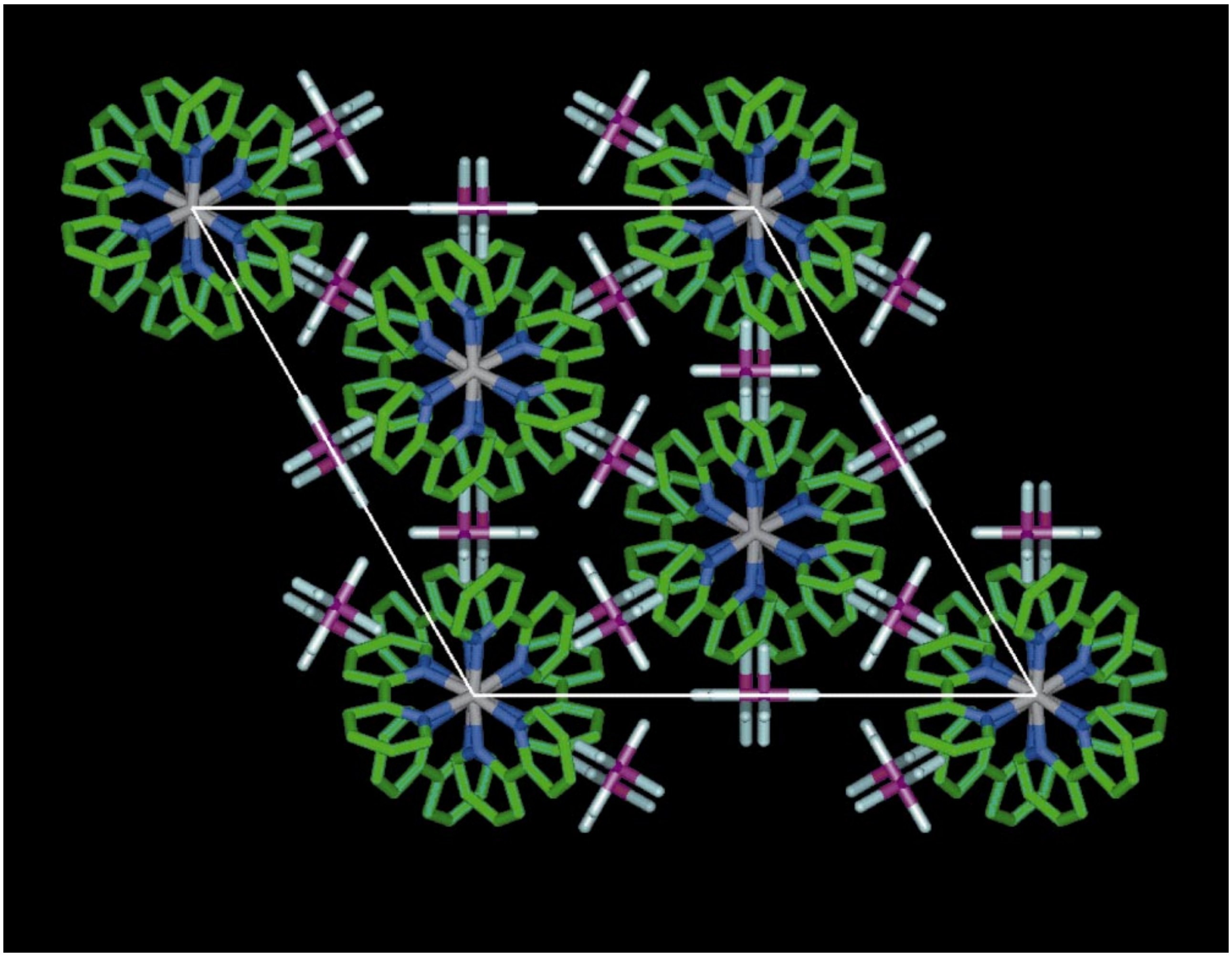
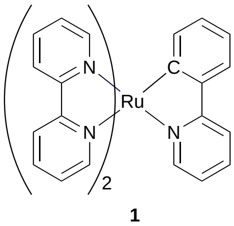


Fig. 8 Three-fold representation of the crystal structure of $[Ru(bipy)_3][PF_6]_3$ [KUFDOE] in space group $R\bar{3}c$ with $a = b = 17.85$, $c = 19.92$; the cations have local D_3 (32) symmetry and the anions have local D_2 (2) symmetry. Colours as for Figs. 5 and 7



1

Crystalline $[Re(bipy)_3][ReO_4]_2$ is isomorphous with $[Ru(bipy)_3][PF_6]_2$ (see Table 1) despite the difference in the geometry of the anions. This is possible because both the octahedral and tetrahedral anions can be oriented with three-fold symmetry aligned to that symmetry in the cell. However, $[Ru(bipy)_3][ClO_4]_2$ and $[Zn(bipy)_3][ClO_4]_2$ crystallise instead in space group *C*2/*c*, despite the fact that the tetrahedral ClO_4^- ion could orient the same way as the ReO_4^- ion. However, both of the perchlorate complexes maintain the columns of cations linked by the SAE motif (see Table 1). The columns of embracing $[M(bipy)_3]^{2+}$ ions deviate slightly from exact linearity, but the M···M distances are essentially the same, at 8.0 and 8.1 Å respectively. The SAE columnar crystal structure of $[Zn(bipy)_3][ClO_4]_2$ is shown in Fig. 9.

Table 2 lists other tris(bidentate ligand) complexes of Fe and

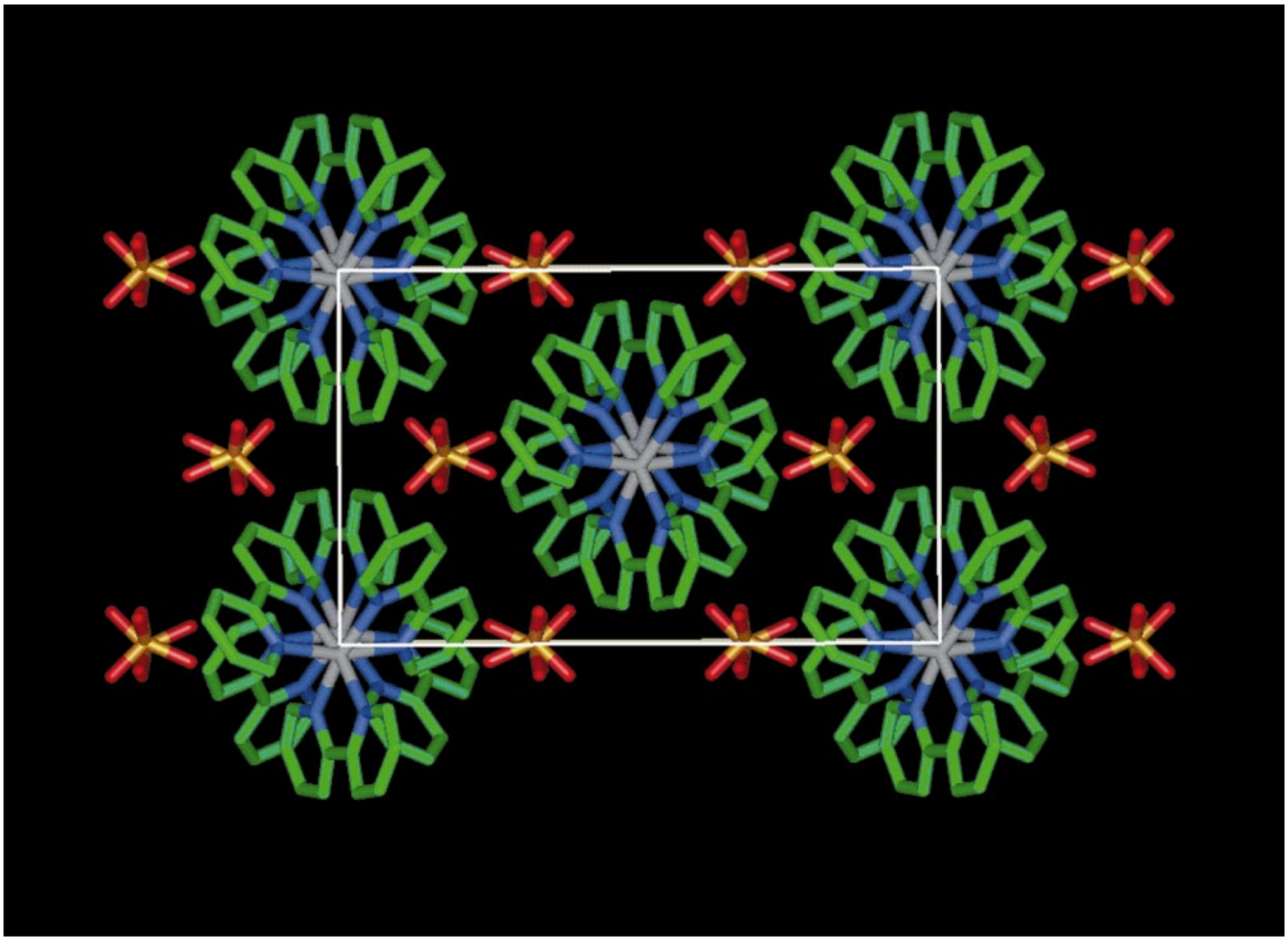


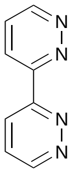
Fig. 9 The columns of cations involved in sextuple aryl embraces in crystalline $[Zn(bipy)_3][ClO_4]_2$ [ZAMGAV02], space group *C*2/*c*. The anions (Cl orange, O red) are disordered, and only one disorder component of each is shown

Table 2 Compounds of type $[M(bipy)_2L'][PF_6]_2$ or $[ML'_3][ClO_4]_2$ (L′ = ligand geometrically similar to bipy) which are isostructural with those in Table 1. The M · · · M distance is *c*/2 in each case

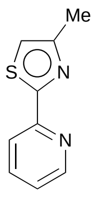
Refcode	Compound *	Space group	Cell dimensions *a*,*c*/Å
COMVIJ	$[Ru(bipy)_2(L^1)][PF_6]_2$	$P\bar{3}c1$	11.0, 16.4
VOCBOE	$[Rh(bipy)_2(L)][PF_6]_2$	$P\bar{3}c1$	10.7, 16.4
SIXJUE	$[Fe(L^2)_3][ClO_4]_2$	$P\bar{3}c1$	10.3, 15.9
FONDER	$[Fe(L^3)_3][ClO_4]_2$	$P\bar{3}c1$	10.2, 17.8
FONDIV	$[Ni(L^3)_3][ClO_4]_2$	$P\bar{3}c1$	10.3, 17.6
VAVSUG	$[Fe(L^4)_3][ClO_4]_2$	$P\bar{3}c1$	10.5, 17.5
VAVTAN	$[Ni(L^4)_3][ClO_4]_2$	$P\bar{3}c1$	10.4, 17.6

* L^1 = 4,5-Diazafluorene; L = 2-(2-pyridyl)phenyl; L^2 = 3,3′-bipyridazine; L^3 = 4-methyl-2-(pyridin-2-yl)-1,3-thiazole; L^4 = 2-(3,5-dimethylpyrazol-1-yl)pyridine.

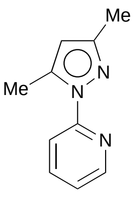
Ni with the related heterocyclic ligands L^2, L^3 and L^4 which crystallise with the same lattice as those in Table 1. In the complexes of the dissymmetric ligands L^3 and L^4 there is two-fold orientational disorder of each chelate, and the crystals also contain disordered anions, but the columnar SAEs in the crystals remain and apparently prevent further orientational disorder of the cations involving misalignment of the three-fold axes.



L^2



L^3



L^4

Chirality of the Sextuple Aryl Embrace

There is another twist to this story of infinite SAEs. Each SAE involves inversion symmetry, which is crystallographic in most of the crystal structures already described, and approximate in the remainder. Consequently enantiomeric $[M(bipy)_3]$ complexes of opposite chirality alternate along the columns of SAE, and resolved $[M(bipy)_3]$ complexes are not able to form an SAE. Fig. 10 shows part of the crystal structure of resolved $[Ru(bipy)_3][ClO_4]_2$ [YUMJOF] which contains two $[Ru(bipy)_3]^{2+}$ complexes of the same chirality in the asymmetric unit of space group *C*2. The homologue $[Zn(bipy)_3][ClO_4]_2$ is isomorphous. Each of the two molecules generates layers of hexagonal arrays of cations: one layer is flat and the other is puckered. The Ru · · · Ru distances are 7.51 and 8.18 Å in the flat layer (Fig. 10), and 8.44 and 8.52 Å in the puckered layer. In the flat layer, the cations form embracing pairs involving four bipy ligands, shown in Fig. 11, which are similar to the orthogonal quadruple phenyl embrace (OQPE) previously described for Ph_4P^+ and which therefore are termed orthogonal quadruple aryl embrace (OQAE). The orthogonality of these embraces is most evident in the orthogonality of the two bipy ligands not involved in the embrace.

An Isolated Sextuple Aryl Embrace

We have located one instance of a non-infinite SAE, in the compound $\{[Ni(bipy)_3]^{2+}\}_2\{[Ag(CN)_2]^-\}_3Cl^-\cdot 10H_2O$ [LEZBUN]. As shown in Fig. 12 these crystals contain columns of · · {$[Ni(bipy)_3]$–SAE–$[Ni(bipy)_3]$} · · {Cl + H_2O} · · {[Ni-

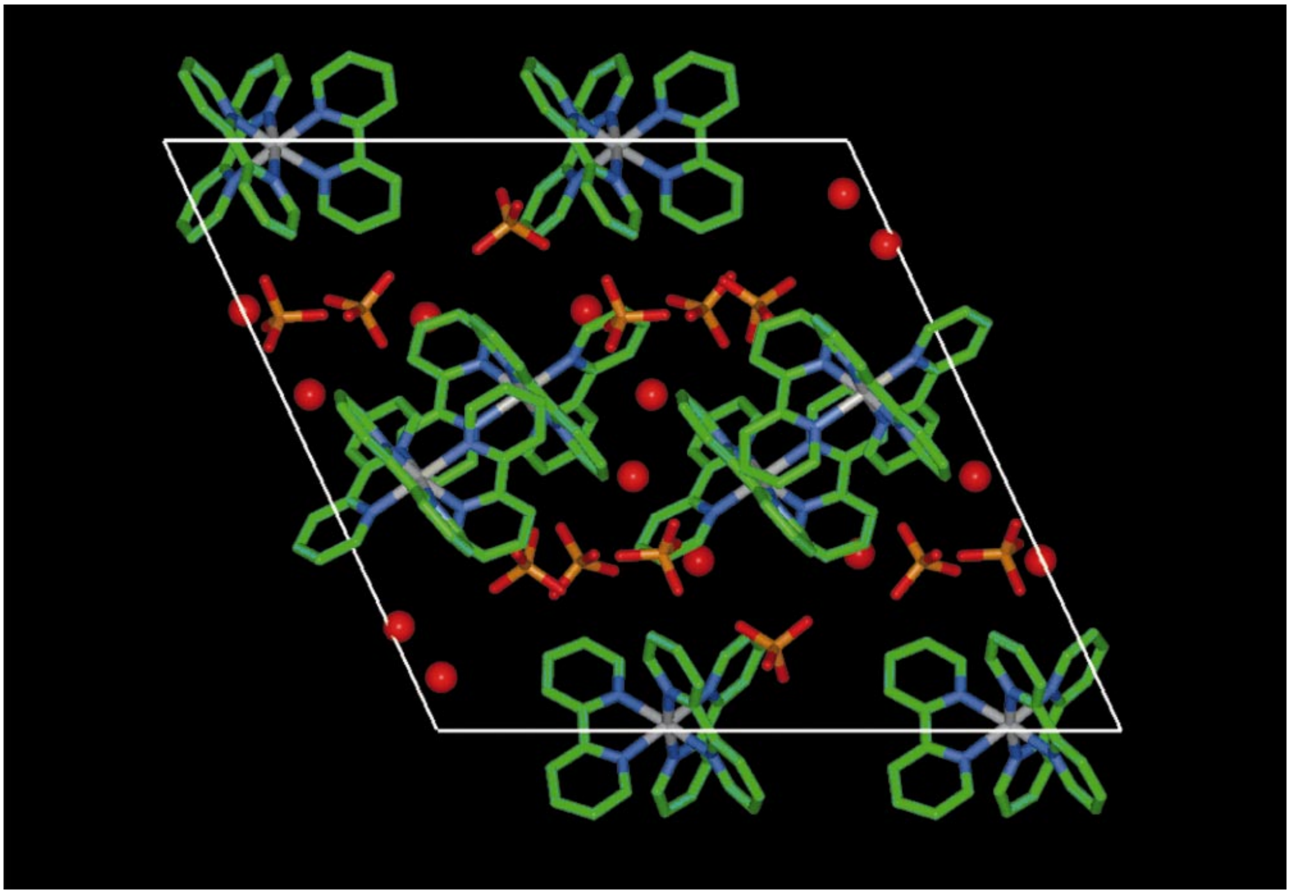


Fig. 10 Part of the crystal structure of the resolved compound [Ru(bipy)$_3$][ClO$_4$]$_2$·H$_2$O [YUMJOF], showing the absence of infinite columns of SAE

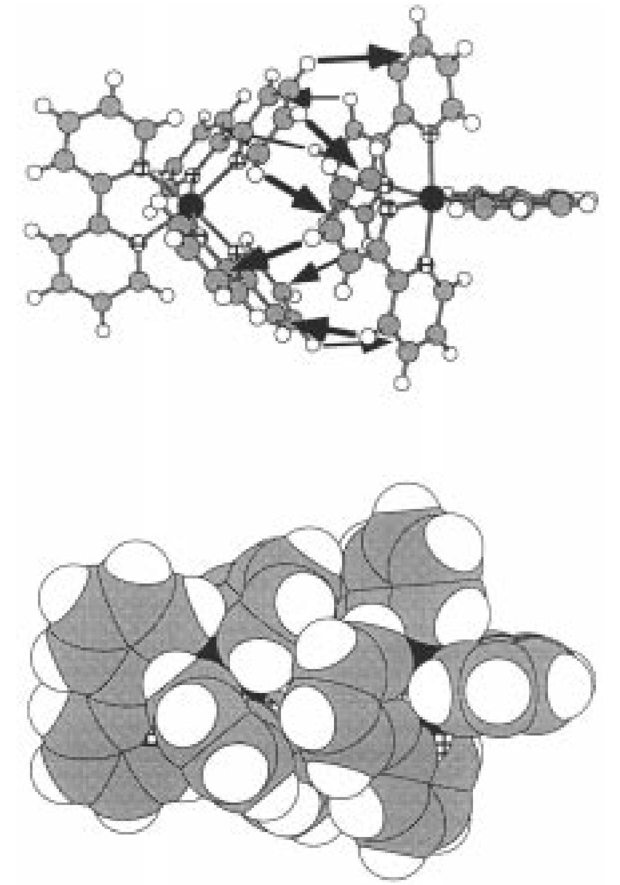


Fig. 11 The orthogonal quadruple aryl embrace involving four bipy ligands between a pair of complexes [Ru(bipy)$_3$]$^{2+}$ in [Ru(bipy)$_3$][ClO$_4$]$_2$·H$_2$O [YUMJOF]. The Ru···Ru distance is 7.5 Å, H···C interactions are marked as arrows

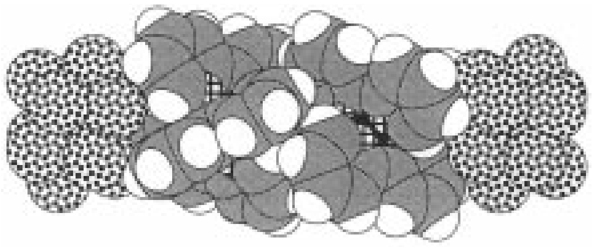


Fig. 12 Part of the crystal structure of {[Ni(bipy)$_3$]$^{2+}$}$_2${[Ag(CN)$_2$]$^-$}$_3$Cl$^-$·10H$_2$O [LEZBUN], showing an isolated SAE between two [Ni(bipy)$_3$]$^{2+}$ in the central region, with aggregates of hydrogen bonded Cl$^-$ and H$_2$O molecules at either end. The Cl$^-$ and H$_2$O are disordered amongst the locations shown by the speckled spheres

(bipy)$_3$]–SAE–[Ni(bipy$_3$)]}··{Cl + H$_2$O}·· {surrounded by [Ag(CN)$_2$]$^-$ ions} in which isolated SAEs are separated by a hydrogen-bonded aggregate of (disordered) Cl$^-$ and H$_2$O. The significance of this crystal packing is the segregation of the embrace domains and the hydrophilic domains.

The Sextuple Aryl Embrace and the Triple Helicates

The triple helicates are oligometal complexes comprised of three ligands each of which contains sequences of flexibly connected bidentate heterocyclic ligands.[2,15–19] Examples of such ligands are L^5 and L^6. For example, the double bidentate ligand L^6 forms bimetallic complexes [M$_2$(L^6)$_3$] in which two adjacent metal atoms each have tris(bidentate) co-ordination.[15,20]

While there are superficial similarities, there is a fundamental stereochemical difference between the triple helicates and a pair of tris(bidentate ligand)metal complexes engaged in sextuple aryl embrace: the tris(bidentate) co-ordinated metal complexes in a triple helicate all have the same chirality, whereas columns of metal complexes in SAE have alternating chirality. The constant chirality of a triple helicate is a consequence of the linked

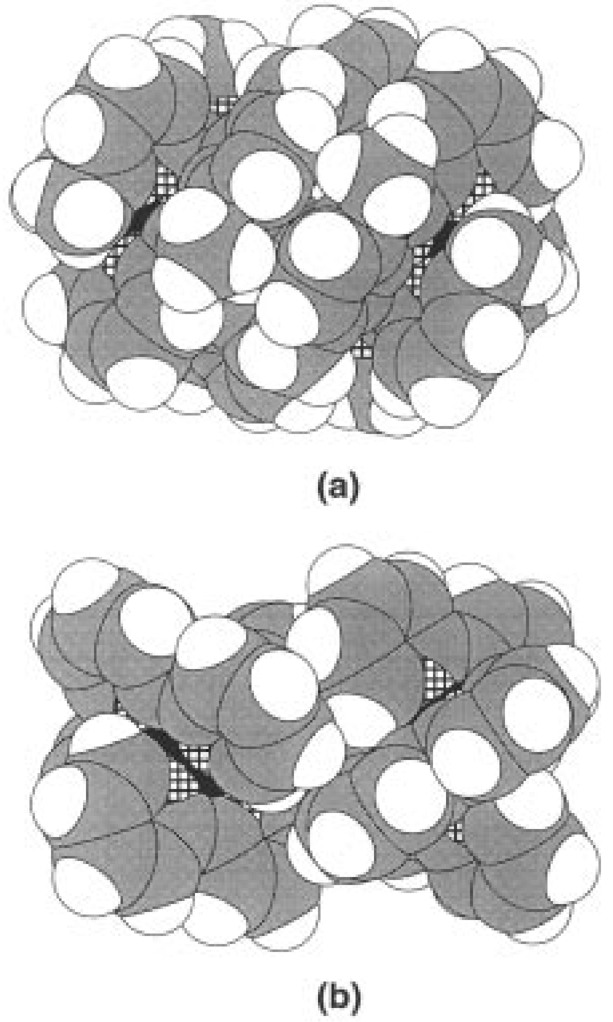
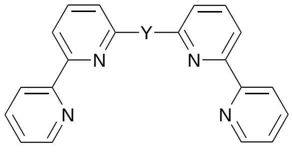
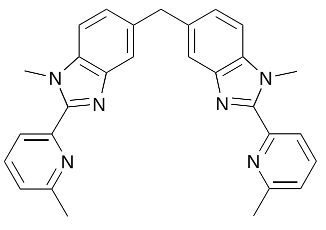


Fig. 13 The contrasted supramolecularity of (a) the triple helicate chelation of two metal atoms by three double bidentate ligands (L^6) and (b) the sextuple aryl embrace. Note the local face-to-face contiguities in the triple helicate structure and the edge-to-face contiguities of the SAE



L^5 Y = CH$_2$OCH$_2$ or CH$_2$CH$_2$



L^6

rigid ligand sections, and means that contiguous planar ligand moieties are approximately parallel and involved in local offset-face-to-face interactions, as illustrated in Fig. 13(a). In contrast, the SAE depends on vertex-to-face local intermolecular interactions, requiring that the planar ligand sections be strongly inclined, as illustrated in Fig. 13(b).

Interaction Energies

We have investigated the intermolecular energy of the SAE between [M(bipy)$_3$] complexes, as the sum of the calculated atom–atom intermolecular energies. Each atom–atom energy is calculated as the van der Waals energy (Lennard–Jones 12-6 function) and the coulombic energy (using a distance dependent permittivity).[2] The results are quite dependent on the partial charges assigned to the atoms, which we have investigated using density functional calculations of the electronic structures of [Ru(bipy)$_3$]^0, [Ru(bipy)$_3$]$^{2+}$ and [Ru(bipy)$_3$]$^{3+}$. The atom partial charges evaluated by the Mulliken, Hirshfeld or electrostatic potential (ESP) methods display variable polarisations which are greatest for the Mulliken method and least for the Hirshfeld method. In general we adopt the ESP results as an average. Using these atom partial charges, shown in Fig. 14, and improved atom–atom parameters for the van der Waals energy,[21] we calculate −14.4 kcal mol^{-1} and 0.0 kcal mol^{-1} for the van der Waals and coulombic energies respectively of the SAE {[Ru(bipy)$_3$]^0}$_2$. For the SAE {[Ru(bipy)$_3$]$^{2+}$}$_2$ at the geometry of crystal structure [BPYRUF10] these energies are −12.6 and +15.0 kcal mol^{-1} respectively, and for the {[Ru(bipy)$_3$]$^{3+}$}$_2$ in [KUFDOE] the values are −4.2 and +24.6 kcal mol^{-1}. It is notable that rather small changes in the atomic partial charges, principally the δ+ charge of H, have substantial influence on the coulombic energies, as a consequence of the large number of H$^{\delta+}\cdots$H$^{\delta+}$ pairs. The sensitivity of the coulombic energies to partial charge assignments reduces confidence in the results, and we are investigating further the calculation of interaction energies in these embraces.

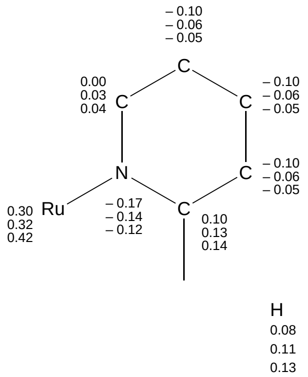


Fig. 14 Atom partial charges derived from density functional calculations and used for the calculation of the intermolecular energies of sextuple aryl embraces for [Ru(bipy)$_3$]^z. The three values for each atom of the asymmetric unit are for $z = 0$, 2+, 3+ respectively, listed downwards

Exceptions

The significance of the SAE as a concerted supramolecular motif for tris(bipyridyl)metal complexes can be assessed through the exceptions to it. The complex [Cu(bipy)$_3$][ClO$_4$]$_2$ [TBPYCU] is triclinic, with columns of cations parallel to *c* and with the Cu$\cdots$Cu distance 7.94 Å. The overall arrangement of columns is pseudo-hexagonal, but the pseudo-three-fold axis of each molecule is not aligned with the column direction. The related crystalline compound [Mn(bipy)$_3$][ClO$_4$]$_2$·0.5H$_2$O [YOWHEX] also does not adopt the SAE motif.

In the Cambridge Structural Database there are about twenty other compounds which contain [M(bipy)$_3$]^z complexes, $z = 2+$, 3+, crystallised with larger and more elaborate anions, such as tartrate, hexacyanometalates, [Cl$_3$FeOFeCl$_3$]$^{2-}$, and various polyoxometalates. These crystallise in a variety of space groups, and frequently with included solvent, and in none of them the three-fold axes of [M(bipy)$_3$] are aligned as an SAE. In general there are other aryl embraces between ligands, but the volume-demanding anions disrupt the SAE, and appear to force the formation of less well packed lattices which therefore include solvent.

Related Multiple Aryl Embraces in Crystalline Tris(Tridentate Ligand) Complexes

Finally, we point out that there are several examples of [M(terpy)$_3$]$^{2+}$ which crystallise in a trigonal lattice very similar

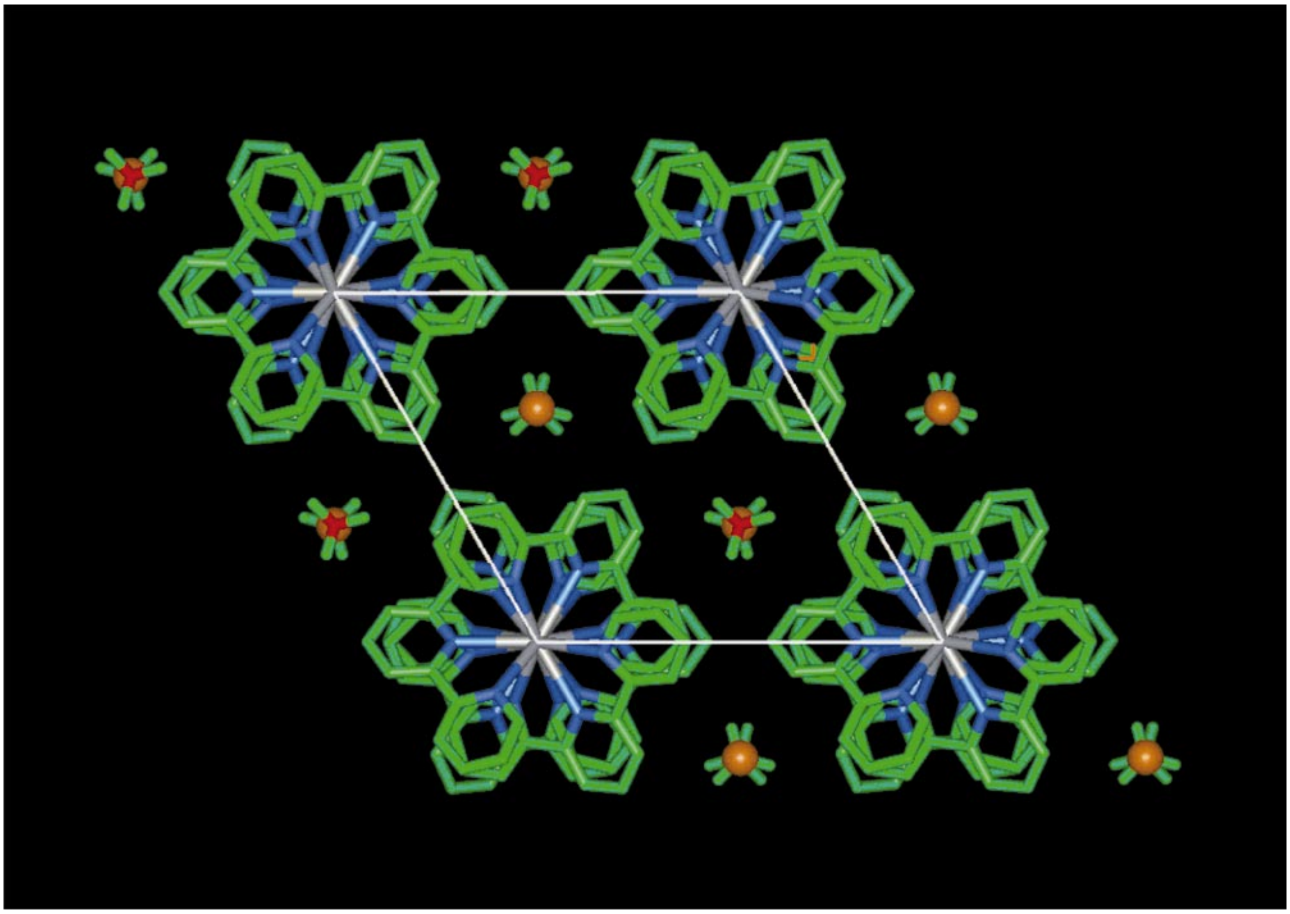


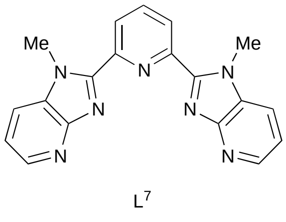
Fig. 15 Three-fold view of the lattice in $[Sr(terpy)_3]Br_2 \cdot CH_3OH$ [TAQKAX]: Sr is silver, Br orange. The Br^- and CH_3OH alternate along three-fold axes and are shown overlapping

Table 3 Crystals containing $[M(terpy)_3]^{2+}$ which occur as linear (or near linear) chains of molecules forming sextuple aryl embraces

Refcode	Compound	Space group	Cell dimensions *a*,*c*/Å
FUYPAQ	$[Pb(terpy)_3][ClO_4]_2$	$P\bar{6}2c$	13.2, 14.7
TAQJOK	$[Ca(terpy)_3]I_2 \cdot 1.7CH_3OH$	$P3c1$	12.9, 15.3
TAQJUX	$[Sr(terpy)_3]I_2 \cdot 1.7CH_3OH$	$P3c1$	13.1, 15.3
TAQKAX	$[Sr(terpy)_3]Br_2 \cdot 2CH_3OH$	$P\bar{3}c1$	13.0, 15.1

to that adopted by the $[M(bipy)_3]^{2+}$ crystals with columnar SAE motifs. These crystals are included in Table 3. Fig. 15 shows the lattice of $[Sr(terpy)_3]Br_2 \cdot 2CH_3OH$ [TAQKAX] which is very similar to that of $[Ru(bipy)_3][PF_6]_2$ (Fig. 5). The sextuple aryl embrace of three terpy ligands on one molecule with three on its neighbour along the three-fold axis is shown in Fig. 16. The nine-fold co-ordination of Sr is appreciably compressed along its three-fold axis, and accordingly the three pyridyl rings which each complex presents to its neighbour comprise a relatively shallow bowl, the intermolecular edge-to-face interactions are oblique, and the Sr···Sr distance is relatively short, at 7.55 Å.

A similar SAE occurs in the compound $[Eu(L^7)_3][ClO_4]_3$ [HANMOY] which crystallises in space group $R\bar{3}$.



L^7

Discussion

The principal result from our analysis of a variety of crystal structures of $[M(bipy)_3]^z$ and related compounds is that even though these complexes and associated anions could conceivably pack in a variety of mutual orientations, with small anions there is one consistent orientation in the packing of the complexes, namely that of the sextuple aryl embrace. These molecules commonly align their molecular three-fold or pseudo-three-fold axes to be parallel, in order to achieve the SAE. Increase in the positive charge *z*, and concomitantly the number of associated anions to be accommodated in the crystal, causes the lattice to expand in various ways, but the SAEs are retained. The M···M distance for a pair of $[M(bipy)_3]^z$ complexes in sextuple aryl embrace is *ca.* 7.7 Å for $z = 0$, and 8.1 ± 0.1 Å for $z = 2$, and it appears that the optimal distance for the SAE is in this distance range. There are but a few crystal structures for $[M(bipy)_3]^{3+}$ with simple anions and there is no evidence of *general* occurrence of the SAE for these more highly charged complexes.

The absence of water or other solvent of crystallisation in the $[M(bipy)_3]^z$ crystals containing the SAE is further evidence of efficient packing in these crystals.

A tris(bipyridyl)metal complex can form two SAEs in opposite directions along its three-fold or pseudo-three-fold axis, and accordingly the SAEs occur as infinite linear (or near linear) chains in crystals. We speculate that oligomers of SAEs could occur in solutions of the complexes tabulated in this paper, and seek evidence for them.

The sextuple aryl embrace of the $[M(bipy)_3]$ complexes and the sextuple phenyl embrace of Ph_3P, Ph_4P^+ and derivatives have similar geometrical properties, with understandable differences. The M···M distance of the SAE is at least 1 Å longer than the P···P distances of SPEs. This is a consequence of the

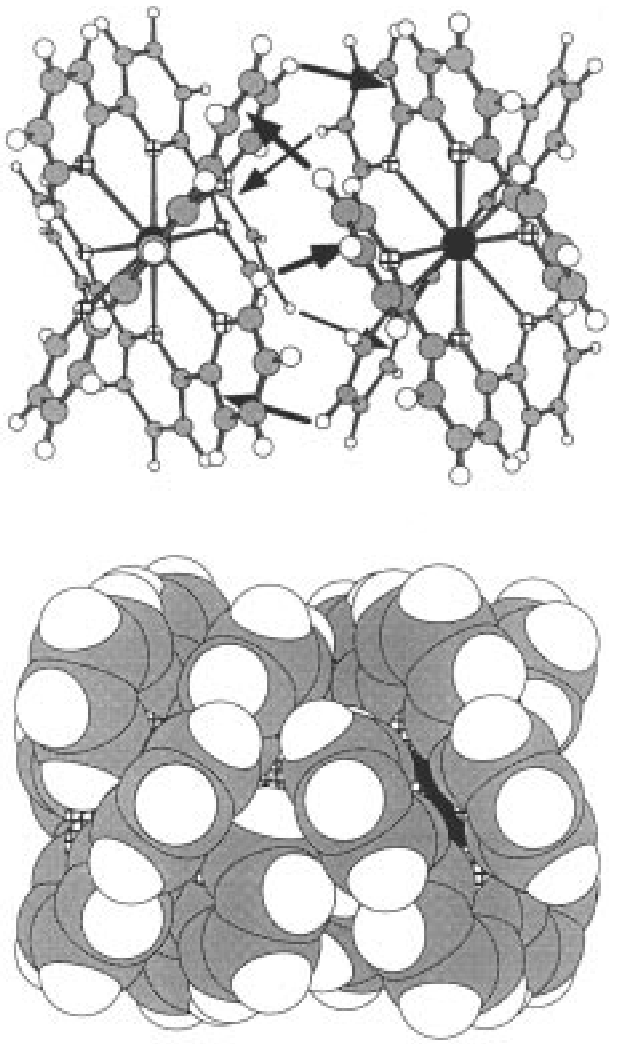


Fig. 16 Skeletal and space-filling representations of the SAE between a pair of $[Sr(terpy)_3]^{2+}$ complexes in [TAQKAX] to show the way in which the rings come together. Six of the influential H···C interactions are marked as arrows

fact that the octahedral geometry at M causes the tris(pyridyl) bowl to be deeper than the Ph_3 bowl (Fig. 1), and the C–H···C interactions of the SAE are aligned more closely to the three-fold axis of the embrace than are the corresponding interactions of the SPE (Fig. 2). In a typical $[Ph_4P^+]_2$ SPE the distances between the centroids of the edge-to-face interacting rings are *ca.* 5 Å, while in $[Ru(bipy)_3]^0$ these distances are in the range 5.1–5.4 Å. Similarly, the geometrical features of the PQAE shown in Fig. 4 are similar to those of the parallel quadruple phenyl embrace, PQPE.[10]

Acknowledgements

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