

# Synthesis of pyridazinyl ligands for multimetallic complexes

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Received (in Montpellier, France) 10th August 2006, Accepted 4th September 2006

First published as an Advance Article on the web 15th September 2006

DOI: 10.1039/b611561f

A family of ligands based upon the linking of two or three bis-(2-pyridyl)pyridazine (dppz) moieties *via* the 4- or 4,5-positions of the pyridazine rings has been synthesised using an inverse electron demand Diels–Alder pathway. Thus, reaction of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (dptz) with a series of dienes (1,4-divinylbenzene, 1,5-cyclooctadiene, norbornadiene, 1,5-hexadiene or 1,4-cyclohexadiene), diketones (1,4-diacetylbenzene), or trienes (*trans,trans,cis*-1,5,9-cyclododecatriene or *trans,trans,trans*-1,5,9-cyclododecatriene) has been studied and seven ligands isolated, namely 4,4'-(1,4-phenylene)bis(3,6-dipyridin-2-ylpyridazine) ( $L^1$ ), 5,6,11,12-tetrahydro-1,4,7,10-tetrapyridin-2-ylcycloocta[1,2-*d*:5,6-*d'*]dipyridazine ( $L^2$ ), 5,10-methano-1,4,6,9-tetrapyridin-2-ylpyridazino[4,5-*g*]phthalazine ( $L^3$ ), 4,4'-ethane-1,2-diylbis(3,6-dipyridin-2-ylpyridazine) ( $L^4$ ), 1,4,6,9-tetrapyridin-2-ylpyridazino[4,5-*g*]phthalazine ( $L^5$ ), cyclododeca[1,2-*d*:5,6-*d'*]dipyridazine-(11*Z*)-5,6,11,12,15,16-hexahydro-1,4,7,10-tetrapyridin-2-yl ( $L^6$ ) and 5,6,11,12,17,18-hexahydro-1,4,7,10,13,16-hexapyridin-2-ylcyclododeca[1,2-*d*:5,6-*d'*:9,10-*d''*]tripyridazine ( $L^7$ ). Compounds  $L^1$ ,  $L^2$  and  $L^4$  have been characterised by single crystal X-ray diffraction revealing the formation of molecular stacking in the solid-state *via*  $\pi$ – $\pi$  interactions between dppz moieties. The potential of these ligands to form multimetallic complexes has been demonstrated by the successful synthesis and structural characterisation of  $\{[Cu_4(L^1)(NO_3)_6(MeO)_2(MeOH)_2]\}$ ,  $\{[Cu_4(L^1)(NO_3)_6(MeO)_2(EtOH)_2]\}$ ,  $\{[Cd(NO_3)(EtOH)_3][Cd(NO_3)_3(L^2)]\}$  and  $\{[Cd(NO_3)_2(L^5)]\}$ .

## Introduction

The synthesis of multimetallic arrays is an area of research that has received considerable attention over recent years due, in part, to potential applications in information storage,<sup>1</sup> magnetic arrays,<sup>2</sup> porous hosts<sup>3</sup> and light-harvesting devices.<sup>4</sup> The synthesis of multimetallic arrays requires careful design of ligands that encourage divergent co-ordination processes, and several successful synthetic protocols have been reported with a variety of ligand types, with perhaps the greatest variety of ligand systems based upon *N*-heterocyclic donor ligands, including polypyridyl systems.<sup>5</sup> Ligands that contain aryl rings with multiple *N*-donor atoms such as pyridazine, pyrazine, and tetrazine can lead to increased proximity of metal cations in multimetallic complexes and may generate enhanced intermetallic interactions. Pyridazine has, therefore, been used for the construction of multimetallic arrays, most notably grids.<sup>6</sup> A variety of synthetic strategies for the preparation of substituted pyridazines has been reported, but perhaps one of the most interesting is *via* reaction of 1,2,4,5-tetrazines with alkenes.<sup>7,8</sup> Indeed, we and others have extensively studied pyridyl-<sup>9</sup> or pyrazinyl-<sup>10,11</sup> substituted 1,2,4,5-tetrazines as ligands for generating multimetallic arrays including co-ordination polymers.

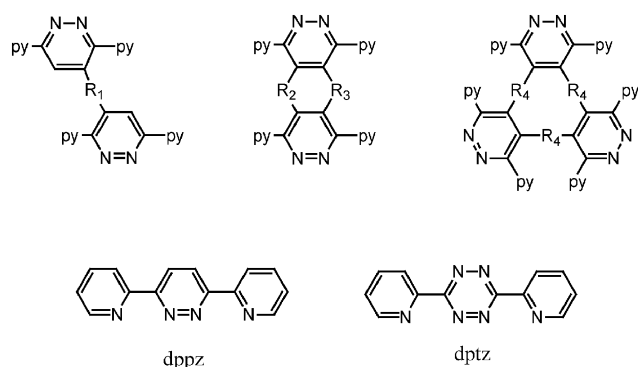
The synthesis of substituted pyridazine derivatives can be performed either *via* heteroaryl-coupling reactions, typically

Stille- or Suzuki-coupling reactions between suitably functionalised aryl groups and dihalopyridazine derivatives,<sup>12</sup> or *via* “inverse electron demand” Diels–Alder reactions with 1,2,4,5-tetrazines.<sup>8</sup> We adopted the latter approach to the synthesis of new pyridazines *via* reaction of 3,6-diaryl-1,2,4,5-tetrazines with alkenes or carbonyl moieties, and report herein the synthesis, and in some instances the structural characterisation, of a set of new ligands that consist of two 3,6-di(2-pyridyl)-1,2-pyridazine (dppz) units separated by a variety of spacers (Scheme 1). In addition, attempts to prepare ligands with more than two dppz groups will be discussed. In all cases, the ligands were synthesised from 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (dptz) through an inverse electron demand Diels–Alder reaction with alkene or carbonyl groups. Finally, some complexation reactions are reported which illustrate the potential of these ligands to generate multimetallic arrays.

## Results and discussion

We have prepared a variety of ligands containing two dppz units *via* Diels–Alder reactions between dptz and a series of dialkenes and diketones. A typical reaction involved stirring of dptz with a dialkene in a 4 : 1 stoichiometry in a non-polar solvent, typically toluene or  $CHCl_3$ . Although the excess of dptz serves primarily to improve the yield of each reaction, it also has the effect of partially dehydrogenating the initial product of reaction. However, this dehydrogenation process was always incomplete, and addition of an oxidising agent such as [bis(trifluoroacetoxy)iodo]benzene was necessary to

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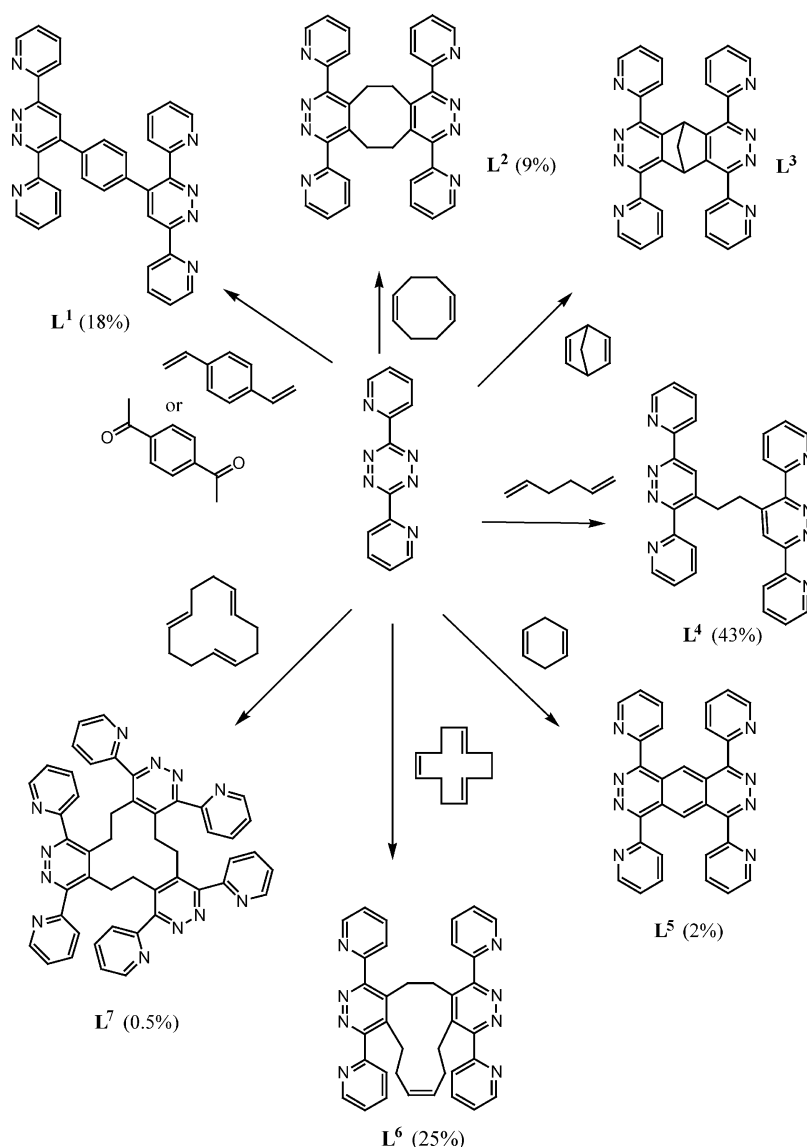
**Scheme 1** Structure of the ligands used in this study.

complete the reaction. The choice of [bis(trifluoroacetoxy)iodo]benzene as oxidant follows a previously described procedure for related compounds.<sup>13</sup> Although other oxidants can be used, such as *ddq*,<sup>8</sup> [bis(trifluoroacetoxy)iodo]benzene was

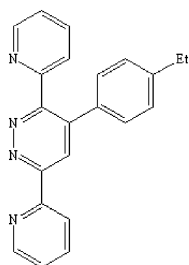
found to be a very clean and efficient reagent in the systems studied. Final products were purified either by column chromatography using acetonitrile or a toluene–acetone mixture (1 : 1) as eluent, or in some instances by precipitation from acetone. The reactions and products for the synthesis of *di*-*dppz* reactions are summarised in Scheme 2.

Reaction of *dptz* with 1,4-divinylbenzene or 1,4-diacetylbenzene affords *L*<sup>1</sup> in some 18% yield. Whereas the reaction using 1,4-divinylbenzene as starting reagent requires oxidation using [bis(trifluoroacetoxy)iodo]benzene, the corresponding reaction with 1,4-diacetylbenzene requires only dehydration using *para*-toluenesulfonic acid.<sup>14</sup> These reactions can be performed under reflux or by stirring at room temperature, and the yields are similar in both cases, but the latter route requires longer reaction times.

*L*<sup>1</sup> was structurally characterised by single crystal X-ray diffraction as discussed below. Commercial 1,4-divinylbenzene can be purchased either in 99% + purity or, more economically,



**Scheme 2** Synthetic approaches to ligands *L*<sup>1</sup>–*L*<sup>7</sup>. All procedures were carried out using toluene as solvent and [bis(trifluoroacetoxy)iodo]benzene as oxidant. Where appropriate, yields are indicated in parentheses for each ligand.



**Scheme 3** By-product  $L^{1a}$  resulting from the reaction between dptz and 4-ethylvinylbenzene.

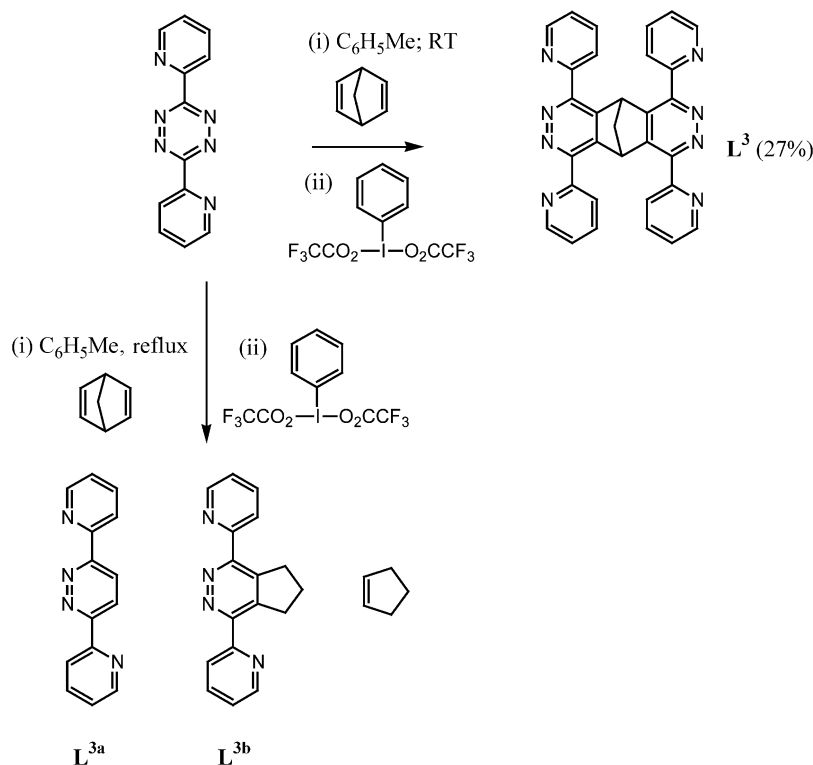
in 80% purity, with the remaining 20% being mostly 4-ethylvinylbenzene. This mixture also affords the desired product  $L^1$ , but in combination with a secondary by-product  $L^{1a}$  (Scheme 3). However, since  $L^{1a}$  can be readily removed from the reaction product by recrystallisation from acetone, this offers the possibility of a more economical route to  $L^1$ .

The preparations of  $L^2$ – $L^5$  proceed similarly *via* reaction of dptz with 1,5-cyclooctadiene (for  $L^2$ ), norbornadiene (for  $L^3$ ), 1,5-hexadiene (for  $L^4$ ) or 1,4-cyclohexadiene (for  $L^5$ ) (Scheme 2). In each case [bis(trifluoroacetoxy)iodo]benzene was used as oxidant to afford the desired di-dppz product. However, certain details of the synthetic procedure merit some elaboration. In the case of  $L^3$ , the reaction can only be carried out successfully at ambient or lower temperature (0 °C is favoured) because competing pathways lead to the formation of different products (Scheme 4). The reactions that produce the two by-products  $L^{3a}$  and  $L^{3b}$  are favoured at higher temperature and involve proton rearrangement followed by cyclopentene elimination. Indeed, refluxing dptz or other 1,2,4,5-tetrazine deri-

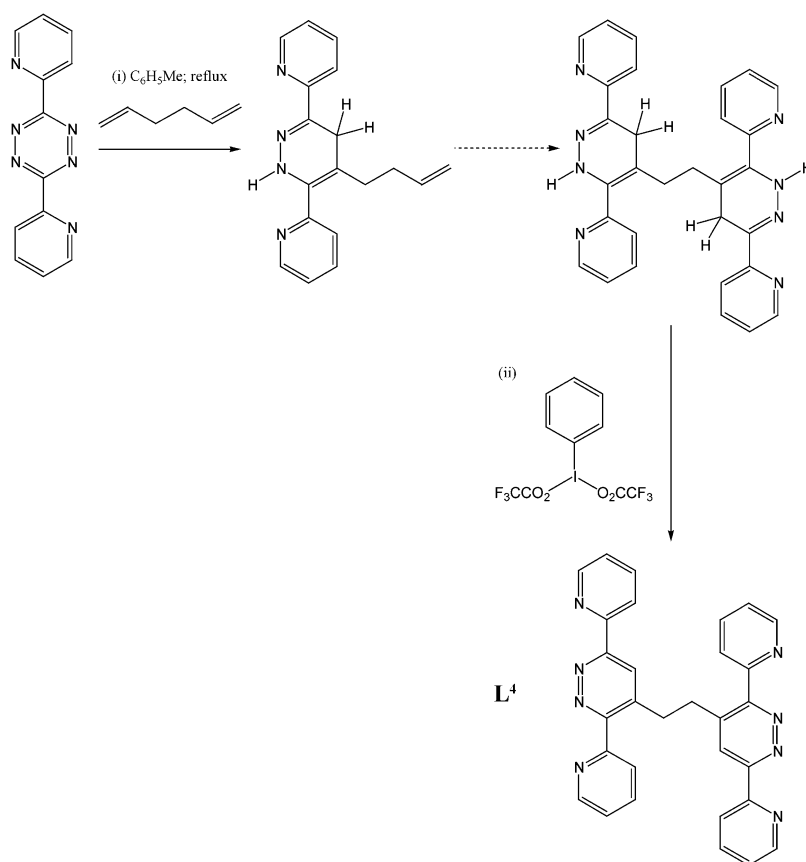
vatives with norbornadiene is an effective synthetic pathway to unsubstituted pyridazine derivatives.<sup>15</sup> The formation of these by-products cannot be completely avoided even at low temperature, and this complicates the purification procedures for  $L^3$ . However, a method that minimises by-product formation is to oxidise the reaction product with [bis(trifluoroacetoxy)iodo]benzene immediately after the initial mixing of the dptz and norbornadiene, thus inhibiting the proton rearrangement required for the formation of  $L^{3a}$  or  $L^{3b}$ . However, it is also important to note that dptz itself can potentially be oxidised to an oxadiazole<sup>16</sup> that similarly has to be separated from the reaction mixture. This means that  $L^3$  only ever forms in very low yield, typically less than 1%, and, although the presence of  $L^3$  in reaction mixtures can be confirmed by  $^1\text{H}$  NMR spectroscopy and by mass spectrometry, our studies confirmed that this synthetic route is, on balance, not viable.

In contrast, the formation of  $L^4$  from dptz and 1,5-hexadiene was found to be successful only under refluxing conditions. The product  $L^4$  was readily extracted and purified by precipitation from acetone. However, when the reaction was carried out by stirring at room temperature and followed by mass spectrometry, a stepwise pathway *via* the formation of mono and the di-substituted products (291  $m/z$  and 499  $m/z$ , respectively) prior to the final oxidation step can be discerned (Scheme 5). We were unable to fully characterise these intermediates which decompose to yield yellow precipitates.

The synthesis of  $L^5$  *via* reaction of dptz with 1,4-cyclohexadiene can be performed under reflux or at room temperature, both reactions leading to the same product in similar yield. In this case, oxidation with [bis(trifluoroacetoxy)iodo]benzene forms the planar tetraazaanthracene species  $L^5$ .



**Scheme 4** Synthesis of  $L^3$ . At room temperature the formation of  $L^3$  is favoured over the formation of the elimination products  $L^{3a}$  and  $L^{3b}$ .

Scheme 5 Stepwise formation of  $L^4$ .

### Attempts to prepare ligands containing three or four dppz moieties

Reaction of dptz with two isomers of 1,5,9-cyclododecatriene, *trans,trans,cis*-1,5,9-cyclododecatriene and *trans,trans,trans*-1,5,9-cyclododecatriene afforded disubstituted  $L^6$  and (in extremely low yield) trisubstituted  $L^7$ , respectively (Scheme 2). The difference in reactivity is linked to 1,5,9-cyclododecatriene having either *trans* or *cis* arrangements of the alkene group. Thus, the di-dppz product  $L^6$  is formed when there are two *trans*-alkenes present in the starting substrate; the third Diels–Alder reaction at the *cis*-alkene of *trans,trans,cis*-1,5,9-cyclododecatriene is then sterically disfavoured resulting in the final isolation of  $L^6$ . Reaction between dptz and cyclooctatetraene afforded an intractable mixture of products which was analysed by mass spectrometry. These experiments indicated that products with up to three dppz moieties had been formed but all attempts to separate the products were unsuccessful in our hands.

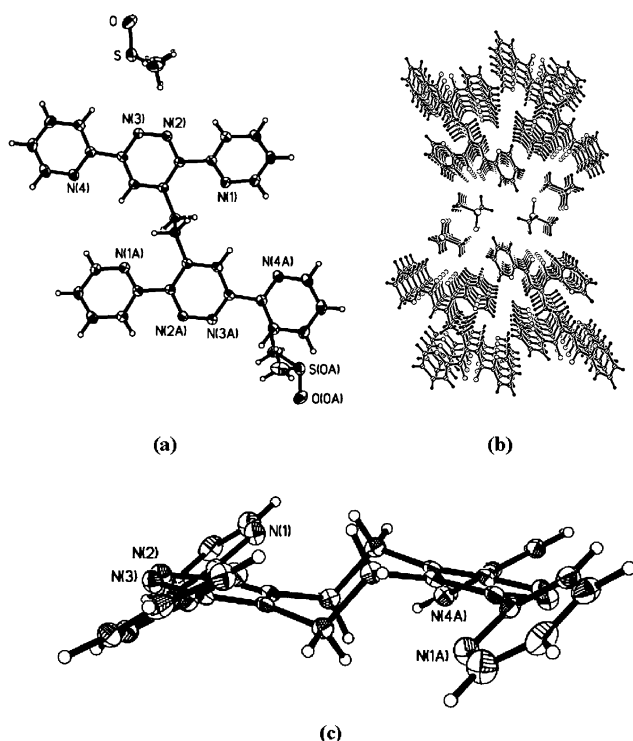
### Single crystal X-ray structures of $L^1$ , $L^2$ and $L^4$

$L^1$  could be crystallised in unsolvated and solvated,  $L^1 \cdot 4CHCl_3$ , forms. The structure of  $L^2$  contains one ligand molecule along with one molecule of chloroform disordered over two positions in each asymmetric unit.  $L^4$  crystallises as a DMSO disolvate (Fig. 1a). All these structures exhibit parallel columns of the dppz-based molecule (Fig. 1b). For  $L^1$ ,  $L^1 \cdot 4CHCl_3$  and  $L^4$ , centroid–centroid distances between pyr-

idine and pyridazine rings were found to be 3.7897(5) Å ( $L^1$ ), 3.779(1) Å ( $L^1 \cdot 4CHCl_3$ ) and 3.8449(3) Å ( $L^4$ ), with dihedral angles of 12.09° ( $L^1$ ), 3.98° ( $L^1 \cdot 4CHCl_3$ ) and 12.84° ( $L^4$ ) confirming the presence of  $\pi$ – $\pi$  interactions within the columns. In the cases of  $L^1$  and  $L^1 \cdot 4CHCl_3$ , the central rings of each ligand are not involved in  $\pi$ – $\pi$  interactions, with centroid–centroid distances of 6.239(2) Å and 7.656(1) Å, respectively. For  $L^2$ , centroid–centroid distances between pyridine rings were measured to be 3.747(7) Å with dihedral angles of 0°. In this case,  $\pi$ – $\pi$  interactions are not located within columns but between adjacent ones. It is worth noting that both molecules  $L^2$  and  $L^4$  adopt a “stair-like” conformation with respect of the central ring with each pyridazine ring on each side of the octyl ring parallel to one another (Fig. 1c).

### Multi-metallic complexes

Reaction of the above ligands with a range of metal salts was investigated. Crystals of  $\{[Cu_4(L^1)(NO_3)_6(MeO)_2](MeOH)_2] \cdot 1.25(CHCl_3) \cdot 0.5(MeOH)\}$ , **1**, were grown by slow diffusion of a solution of  $L^1$  in  $CHCl_3$  with a solution of  $Cu(NO_3)_2 \cdot 2.5H_2O$  in MeOH. Crystals of  $\{[Cu_4(L^1)(NO_3)_6(MeO)_2(EtOH)_2] \cdot 1.2(CHCl_3)\}$ , **2**, were grown by slow diffusion of solutions of  $L^1$  dissolved in  $CHCl_3$  with  $Cu(NO_3)_2 \cdot 2.5H_2O$  in MeOH in the presence of sodium trimesate dissolved in EtOH. The crystal structures of **1** and **2** are very similar except that the terminal co-ordinated MeOH ligands in **1** are replaced by EtOH ligands in **2**.



**Fig. 1** (a) View of the single crystal X-ray structure of  $L^4$  which crystallises as a DMSO disolvate; (b) formation of stacks of ligands via  $\pi$ - $\pi$  interactions between dppz moieties; (c) view of  $L^2$  illustrating the chair-type conformation adopted by the central eight-membered ring in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

(Fig. 2). Selected bond lengths and angles for **1** and **2** are given in Table 1.

The structure of **1** comprises a single molecule of  $L^1$  surrounded by four Cu(II) centres, two at each end of  $L^1$  (Fig. 2a). Two of the Cu(II) cations have square-based pyramidal geometries and are bound to two *N*-pyridyl/*N*-pyridazine donors, one nitrate anion and one bridging methoxide at the square-base with a nitrate anion at the axial position (Fig. 2c,d). In contrast, the two other Cu(II) centres have a similar square-based pyramidal co-ordination sphere but with a MeOH bound at the axial site instead of a nitrate anion. Moreover, for these two Cu(II) centres there are long-range interactions to nitrate anion,  $\text{Cu} \cdots \text{O} = 2.551(5), 2.658(5) \text{ \AA}$  with the methoxide group on each side of  $L^1$  bridging between two Cu(II) cations. The contents of each crystallographic asymmetric unit are completed by solvent chloroform molecules distributed over two partially-occupied sites, and by solvent methanol molecules over one partially occupied site, neither of which interact with the metal centres. As only a single molecule of  $L^1$  is bound to each Cu(II) cation the structure is discrete and not polymeric. A related structure of a Cu(II) complex of the ligand 3,6-bis(2-pyridyl)-pyridazine similarly exhibits a bridging oxygen ligand between two Cu(II) cations, which are in turn co-ordinated to the two bidentate co-ordination sites of the bis-pyridylpyridazine ligand.<sup>17</sup>

The complex  $\{[\text{Cd}(\text{NO}_3)(\text{EtOH})_3][\text{Cd}(\text{NO}_3)_3(L^2)]\}$ , **3**, was obtained by reaction of  $L^2$  with  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and single crystals of **3** were grown by slow diffusion of ethanolic

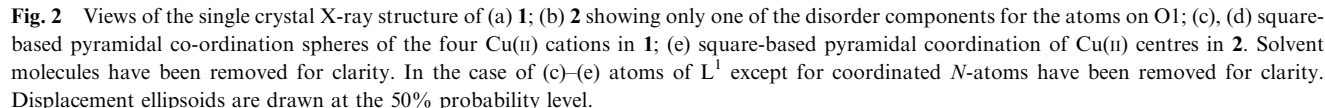
solutions of the metal salt and  $L^2$  in a reaction stoichiometry for Cd :  $L^2$  of 4 : 1. In contrast to the structure of unco-ordinated  $L^2$ , in **3** the ligand does not adopt a “stair” conformation for the central eight-membered ring but rather a “boat” conformation with each of the dppz moieties approaching one another (Fig. 3). The centroid-centroid distance between the two pyridazine rings is  $3.930(4) \text{ \AA}$  with a dihedral angle of  $52.66^\circ$ . Two of the four dimethylene carbon atoms inside the eight-membered ring are slightly strained with larger C-C-C angles of  $115.3^\circ$  and  $115.6^\circ$ , when compared to the angles observed in the crystal structure of  $L^2$  which are  $112.5^\circ$  and  $113.9^\circ$ . The complex consists of a single molecule of  $L^2$  bound to two Cd(II) cations that occupy co-ordination sites that are diametrically opposite one another on the ligand, which is folded in a *syn* arrangement. Two different Cd(II) environments are observed [Fig. 3(b); Table 2] with Cd(1) adopting a hepta-co-ordinate environment bound by two *N*-pyridyl/*N*-pyridazine donors, three ethanol molecules and one bidentate nitrate anion (Fig. 3b). The other Cd(II) cation, Cd(2) is octa-co-ordinate with two *N*-pyridyl/*N*-pyridazine donors and three bidentate nitrate anions. The asymmetric nature of **3** means that Cd(1) and the nitrate anion co-ordinated to it have a formal monopositive charge whereas Cd(2) and the three nitrate anions co-ordinated to it are formally mono-negatively charged. Thus, **3** is zwitterionic which in part explains the somewhat surprising boat conformation observed for the central eight-membered ring of  $L^2$ .

A second  $\text{Cd}(\text{NO}_3)_2$ -based complex has been obtained by the growth of single crystals of  $\{[\text{Cd}(\text{NO}_3)_2(L^5)_3]\}$ , **4**, from the slow diffusion of a solution of  $L^5$  in  $\text{CHCl}_3$  into a solution of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in MeOH in a reaction stoichiometry for Cd :  $L^5$  of 4 : 1. The structure of **4** contains discrete complexes that consist of three molecules of  $L^5$  bridged by two Cd(II) centres (Fig. 4). The two Cd(II) cations are related by symmetry and sit in a distorted cubic co-ordination sphere with four *N*-pyridyl/*N*-pyridazine donors and two bidentate nitrate anions (Table 2). Within each complex, centroid-centroid distances between pyridazine rings are  $3.412(1) \text{ \AA}$  with a dihedral angle between aromatic rings of  $12.18^\circ$ , thus indicating strong  $\pi$ - $\pi$  interactions. Between adjacent complexes, the centroid-centroid distances of  $3.653(1) \text{ \AA}$  between pyridazine rings and a dihedral angle between aromatic rings of  $1.12^\circ$ , reveal weaker  $\pi$ - $\pi$  interactions.

## Conclusions

We have demonstrated the successful synthesis of ligands containing two dppz units joined by a variety of organic linkers. The ligands have been prepared by the reaction of the 1,2,4,5-tetrazine group of dptz with a range of dienes, or in one instance a diketone. In addition, we have explored the possibility of preparing ligands containing three or four dppz moieties, but we encountered either very low yields or no reaction when incorporating more than two dppz groups into our targets. Thus *trans,trans,trans*-1,5,9-cyclododecatriene reacts with dptz to form the desired tri-dppz product in less than 1% yield, and *cis,trans,trans*-1,5,9-cyclododecatriene did not form any tri-dppz product but only the di-dppz species. Solid-state structural characterisation was carried out for some of





Reactions with  $\text{Cu}(\text{NO}_3)_2$  or  $\text{Cd}(\text{NO}_3)_2$  gave rise to discrete metal complexes containing either four  $\text{Cu}(\text{II})$  or two  $\text{Cd}(\text{II})$  cations. The  $\text{Cu}(\text{II})$  centres incorporate a bridging methoxide or ethoxide group between metal cations in adjacent bidentate sites of the dppz groups. In contrast, for  $\text{Cd}(\text{II})$  complexes, only one of the bidentate sites on each dppz moiety is occupied. No examples of co-ordination polymers have been observed using these ligands, despite the choice of metal centres known to commonly adopt polymeric structures.<sup>18</sup> The facile synthesis of ligands containing two dppz moieties from readily available tetrazine starting materials makes them an attractive and potentially highly versatile family of ligands that may be developed for supramolecular chemistry of multi-metallic arrays. We are currently seeking to expand the chemistry reported here.

Starting materials were purchased from Aldrich Chemical Company or from Lancaster Synthesis and were used without further purification. 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine was prepared following the literature procedure.<sup>10</sup> Elemental ana-

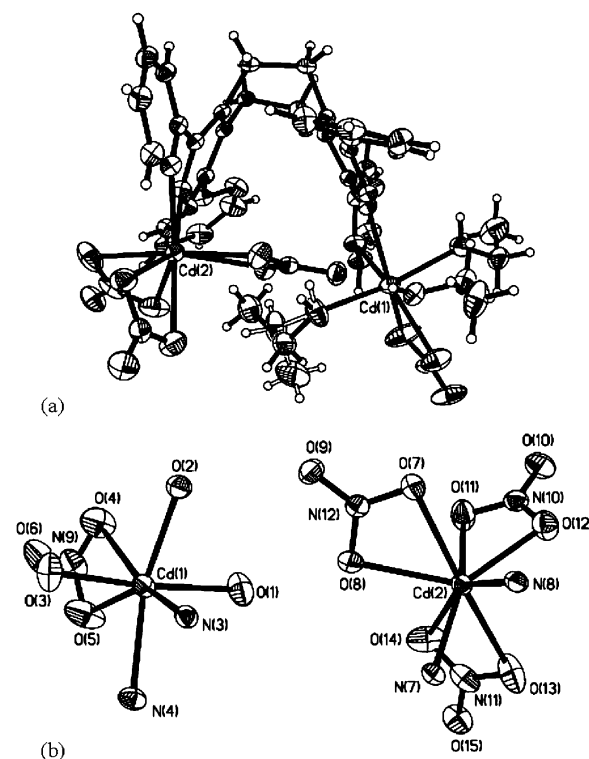
**4,4'-(1,4-Phenylene)bis(3,6-dipyridin-2-ylpyridazine) L<sup>1</sup>.** Dptz (0.5 g, 2.12 mmol) was dissolved in toluene (10 cm<sup>3</sup>) to give a deep red solution and 1,4-divinylbenzene (0.1 cm<sup>3</sup>, 0.7 mmol) was added to the red solution which was heated under reflux and turned yellow overnight. After 16 h [bis(trifluoroacetoxy)iodo]benzene (0.7 g, 1.65 mmol) was added and the solution was heated under reflux for a further 20 min during which time the reaction mixture turned black. After cooling to room temperature aqueous 1 M NaOH (15 cm<sup>3</sup>) was added and a viscous black oil formed. The solution was removed and the black oil was redissolved by stirring with acetone (20 cm<sup>3</sup>) at room temperature. The black solution was then left to stand overnight, and the yellow precipitate which formed was collected, washed with acetone and dried. The product was recrystallised from acetone to give a yellow powder (yield 70 mg, 18%). Alternatively, the product can be purified by

**Table 1** Selected bond length (Å) and angles (°) with s.u.'s for **1** and **2**

<b>For 1</b>			
Cu(1)–O(1)	1.921(4)	O(1)–Cu(1)–N(2)	87.67(18)
Cu(1)–N(2)	1.992(5)	O(1)–Cu(1)–O(4)	98.47(18)
Cu(1)–O(4)	1.995(4)	N(2)–Cu(1)–N(1)	79.7(2)
Cu(1)–N(1)	2.001(5)	O(1)–Cu(1)–O(2)	91.16(18)
Cu(1)–O(2)	2.309(5)	N(1)–Cu(1)–O(2)	91.6(2)
Cu(2)–O(1)	1.912(4)	O(1)–Cu(2)–O(8)	96.58(18)
Cu(2)–O(8)	1.955(4)	O(1)–Cu(2)–N(3)	89.05(18)
Cu(2)–N(4)	1.992(5)	N(4)–Cu(2)–N(3)	78.99(19)
Cu(2)–N(3)	1.996(5)	O(1)–Cu(2)–O(10)	93.24(19)
Cu(2)–O(10)	2.387(5)	N(3)–Cu(2)–O(10)	84.71(19)
Cu(3)–O(12)	1.898(4)	O(12)–Cu(3)–N(6)	88.61(18)
Cu(3)–N(5)	1.987(5)	N(5)–Cu(3)–N(6)	78.4(2)
Cu(3)–N(6)	2.006(5)	O(12)–Cu(3)–O(18)	97.5(2)
Cu(3)–O(18)	2.012(5)	N(6)–Cu(3)–O(18)	144.2(2)
Cu(3)–O(16)	2.200(6)	O(12)–Cu(3)–O(16)	99.9(2)
Cu(4)–O(12)	1.902(4)	O(12)–Cu(4)–N(7)	88.16(19)
Cu(4)–N(7)	1.984(5)	O(12)–Cu(4)–O(21)	97.82(19)
Cu(4)–O(21)	2.006(4)	N(7)–Cu(4)–N(8)	78.9(2)
Cu(4)–N(8)	2.007(5)	O(12)–Cu(4)–O(13)	95.1(2)
Cu(4)–O(13)	2.215(5)	N(7)–Cu(4)–O(13)	116.0(2)
<b>For 2</b>			
Cu1–N1	1.975(5)	Cu2–N3	2.008(5)
Cu1–N2	2.004(5)	Cu2–N4	2.005(6)
Cu1–O2	1.973(4)	Cu2–O9	1.972(4)
Cu1–O4	2.332(5)	Cu2–O10	1.912(4)
Cu1–O10	1.904(4)	Cu2–O11	2.279(5)
O10–Cu1–O2	96.66(18)	O10–Cu2–O9	98.46(19)
O10–Cu1–N1	162.7(2)	O10–Cu2–N4	167.68(18)
O2–Cu1–N1	97.9(2)	O9–Cu2–N4	93.3(2)
O10–Cu1–N2	89.01(18)	O10–Cu2–N3	88.49(18)
O2–Cu1–N2	166.98(19)	O9–Cu2–N3	168.3(2)
N1–Cu1–N2	78.8(2)	N4–Cu2–N3	79.3(2)
O10–Cu1–O4	92.07(19)	O10–Cu2–O11	88.71(19)
O2–Cu1–O4	81.43(18)	O9–Cu2–O11	96.7(2)
N1–Cu1–O4	99.28(19)	N4–Cu2–O11	93.6(2)
N2–Cu1–O4	86.67(19)	N3–Cu2–O11	92.8(2)

column chromatography (silica gel 60, 5 cm column, diameter 2 cm, acetone). Found (calc. for  $C_{34}H_{22}N_8 \cdot H_2O$ ) (%): C 72.64 (72.84), H 4.15 (4.31), N 19.89 (19.99).  $^1H$ -NMR ( $CDCl_3$ ,  $\delta$ /ppm,  $J$ /Hz): 8.83 (m, 2H,  $J = 7.9$ ), 8.78 (m, 2H,  $J = 3.9$ ,  $J = 1.5$ ), 8.70 (s, 2H), 8.52 (m, 2H,  $J = 5$ ), 8.00–7.94 (m, 4H), 7.86 (m, 2H,  $J = 7.8$ ,  $J = 1.8$ ), 7.47 (m, 2H,  $J = 7.4$ ,  $J = 4.2$ ,  $J = 1.3$ ), 7.34 (m, 2H,  $J = 7.1$ ,  $J = 4.3$ ,  $J = 1.2$ ), 7.26 (s, 4H).  $^{13}C$ -NMR ( $CDCl_3$ ,  $\delta$ /ppm): 158.19, 157.77, 155.57, 153.30, 149.48, 149.01, 145.16, 139.91, 137.46, 137.14, 136.90, 129.12, 125.66, 125.02, 124.98, 123.63, 122.10. IR  $\nu/cm^{-1}$ : 3286m, 1636s, 1582s, 1510m, 1475s, 1442m, 1428m, 1408s, 1385s, 1302m, 1285w, 1276w, 1253s, 1152w, 1098s, 1053m, 1040w, 1019w, 990s, 968w, 932s, 903m, 853w, 839s, 815w, 797s, 765m, 748m, 730m, 651m, 620m, 539m, 529w. Mass spec found (calc. For  $C_{34}H_{22}N_8$ ) (ES,  $MH^+$ ): 543.2044 (543.2040).

**Alternative preparation of  $L^1$  at room temperature.** Dptz (0.5 g, 2.12 mmol) was dissolved in toluene (10  $cm^3$ ) to give a deep red solution. 1,4-Divinylbenzene (0.1  $cm^3$ , 0.7 mmol) was added to the red solution and stirred at room temperature for two weeks over which period the solution became orange. [Bis(trifluoroacetoxy)iodo]benzene (0.7 g, 1.65 mmol) was added and the solution stirred for 1 h. Aqueous 1 M NaOH (15  $cm^3$ ) was added to the black solution to form a viscous black oil. The black oil was extracted using the same method



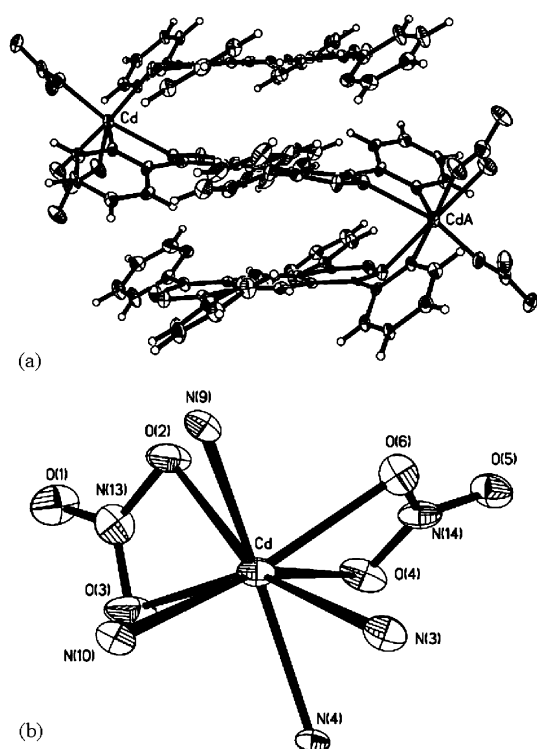
**Fig. 3** (a) View of the structure of **3** illustrating the unusual boat conformation and showing only one of the disorder components for the atoms on O1; (b) view of the two Cd(II) coordination spheres in **3**. Atoms of  $L^2$  except for coordinated  $N$ -atoms have been removed for clarity. Displacement ellipsoids are drawn at the 50% probability level.

as described above to afford  $L^1$  as a yellow powder (yield 70 mg, 12%).

**Alternative preparation of  $L^1$  using 1,4-diacetylbenzene.** Dptz (0.2 g, 0.85 mmol) was dissolved in  $CH_2Cl_2$  (10  $cm^3$ ) to give a deep red solution. 1,4-Diacetylbenzene (60 mg, 0.37 mmol) and *para*-toluenesulfonic acid (880 mg, 5.12 mmol) were added to the red solution, which was heated under reflux for 2 d. After removing the solvent a black solid was recovered. This solid was dissolved in a mixture of  $CHCl_3$  (10  $cm^3$ ) and aqueous 1 M NaOH (10  $cm^3$ ). The  $CHCl_3$  phase was collected and the solvent removed by evaporation. Acetone (15  $cm^3$ ) was added to the residue and the resultant precipitate was collected, washed with acetone and dried to give  $L^1$  as a yellow/brown powder (yield 50 mg, 11%).

Colourless crystals of  $L^1$  were grown from a hydrothermal reaction at 130 °C for 5 d in a sealed steel autoclave in the presence of  $Cd(NO_3)_2 \cdot 4H_2O$ . Crystals of  $L^1 \cdot 4CHCl_3$  were grown from a solution in deuterated chloroform in a sealed NMR tube, which had been left undisturbed for three weeks. After complete evaporation of the solvent, colourless needles suitable for X-ray diffraction were formed.

**5,6,11,12-Tetrahydro-1,4,7,10-tetrapyridin-2-ylcycloocta[1,2- $d'$ ]dipyridazine.  $L^2$ .** Dptz (1 g, 4.14 mmol) was dissolved in toluene (10  $cm^3$ ) to give a deep red solution. 1,5-Cyclooctadiene (0.2  $cm^3$ , 1.63 mmol) was added to the red solution,



**Fig. 4** (a) View of the structure of **4** showing  $\text{Cd}(\text{NO}_3)_2$  moieties linking parallel molecules of  $\text{L}^5$ ; (b) view of the distorted cubic  $\text{Cd}(\text{II})$  coordination sphere observed in **4**. Atoms of  $\text{L}^5$ , except for coordinated  $\text{N}$ -atoms, have been removed for clarity. Displacement ellipsoids are drawn at the 50% probability level.

which was heated under reflux for 3 h over which period the solution turned yellow. [Bis(trifluoroacetoxy)iodo]benzene (1 g, 2.36 mmol) was added to the solution, which was heated under reflux for a further 10 min until the solution turned black. The solution was allowed to cool to room temperature and aqueous 1 M NaOH (20  $\text{cm}^3$ ) was added. The reaction solvent was removed and the viscous black oil was redissolved in acetone (20  $\text{cm}^3$ ). The black solution was left to stand overnight and the yellow precipitate which formed was collected, washed with acetone and dried to give a pale yellow powder (yield 100 mg, 9.4%). The crystal structure of  $\text{L}^2$  was determined from crystals grown by slow evaporation from a  $\text{CHCl}_3$  solution of  $\text{L}^2$ . Found (calc. for  $\text{C}_{32}\text{H}_{24}\text{N}_8$ ) (%): C 73.28 (73.83), H 4.60 (4.65), N 21.41 (21.52).  $^1\text{H}$ -NMR (in  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ,  $J/\text{Hz}$ ): 8.30 (m, 4H,  $J = 4.5$ ), 7.83 (m, 4H,  $J = 7.8$ ), 7.76 (m, 4H,  $J = 7.8$ ,  $J = 1.8$ ), 7.30 (m, 4H,  $J = 4.8$ ,  $J = 1.4$ ), 3.63 (s, 8H).  $^{13}\text{C}$ -NMR (in  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 158.84, 156.59, 147.93, 140.07, 136.70, 125.32, 123.15, 28.95. IR  $\nu/\text{cm}^{-1}$ : 3458m, 1634w, 1586w, 1384s, 1107w, 992w, 836m, 792m, 745m, 729w, 694w, 677w, 667w, 616w. Mass spec found (calc. for  $\text{C}_{32}\text{H}_{24}\text{N}_8$ ) (ES,  $\text{MH}^+$ ): 521.2201 (521.2197).

**5,10-Methano-1,4,6,9-tetrapyridin-2-ylpyridazino[4,5-g]phthalazine.  $\text{L}^3$ .** Dptz (1 g, 4.14 mmol) was dissolved in dry toluene (7  $\text{cm}^3$ ) to give a deep red solution. Norbornadiene (0.15  $\text{cm}^3$ , 1.9 mmol) and [bis(trifluoroacetoxy)iodo]benzene (2 g, 4.72 mmol) were added to the solution which turned black. The solution was left to stir at room temperature for 3 d, after

**Table 2** Selected bond length ( $\text{\AA}$ ) and angles ( $^\circ$ ) with s.u.'s for **3** and **4**

<b>For 3</b>			
$\text{Cd}(1)-\text{O}(2)$	2.3131(19)	$\text{O}(2)-\text{Cd}(1)-\text{N}(3)$	85.44(7)
$\text{Cd}(1)-\text{N}(3)$	2.315(2)	$\text{N}(3)-\text{Cd}(1)-\text{O}(1)$	88.20(8)
$\text{Cd}(1)-\text{O}(1)$	2.319(2)	$\text{N}(3)-\text{Cd}(1)-\text{O}(3)$	81.62(7)
$\text{Cd}(1)-\text{O}(3)$	2.3316(19)	$\text{O}(5)-\text{Cd}(1)-\text{O}(4)$	52.81(8)
$\text{Cd}(1)-\text{O}(5)$	2.332(2)	$\text{N}(3)-\text{Cd}(1)-\text{N}(4)$	68.66(7)
$\text{Cd}(1)-\text{O}(4)$	2.437(2)	$\text{O}(1)-\text{Cd}(1)-\text{N}(4)$	96.62(8)
$\text{Cd}(1)-\text{N}(4)$	2.464(2)	$\text{O}(4)-\text{Cd}(1)-\text{N}(4)$	130.10(7)
$\text{Cd}(2)-\text{N}(7)$	2.3453(19)	$\text{N}(7)-\text{Cd}(2)-\text{N}(8)$	69.14(7)
$\text{Cd}(2)-\text{N}(8)$	2.349(2)	$\text{N}(7)-\text{Cd}(2)-\text{O}(12)$	143.28(7)
$\text{Cd}(2)-\text{O}(12)$	2.350(2)	$\text{O}(12)-\text{Cd}(2)-\text{O}(11)$	53.11(7)
$\text{Cd}(2)-\text{O}(14)$	2.367(2)	$\text{N}(8)-\text{Cd}(2)-\text{O}(7)$	80.34(7)
$\text{Cd}(2)-\text{O}(11)$	2.452(2)	$\text{O}(8)-\text{Cd}(2)-\text{O}(7)$	51.58(6)
$\text{Cd}(2)-\text{O}(8)$	2.464(2)	$\text{N}(7)-\text{Cd}(2)-\text{O}(13)$	74.62(8)
$\text{Cd}(2)-\text{O}(7)$	2.481(2)	$\text{N}(8)-\text{Cd}(2)-\text{O}(13)$	102.50(8)
$\text{Cd}(2)-\text{O}(13)$	2.556(3)	$\text{O}(14)-\text{Cd}(2)-\text{O}(13)$	52.06(8)
<b>For 4</b>			
$\text{Cd}-\text{N}(4)$	2.307(5)	$\text{N}(9)-\text{Cd}-\text{O}(2)$	76.09(17)
$\text{Cd}-\text{O}(6)$	2.325(4)	$\text{O}(3)-\text{Cd}-\text{O}(2)$	53.24(16)
$\text{Cd}-\text{N}(9)$	2.327(5)	$\text{N}(4)-\text{Cd}-\text{N}(3)$	67.75(18)
$\text{Cd}-\text{O}(3)$	2.390(5)	$\text{O}(6)-\text{Cd}-\text{N}(3)$	82.17(16)
$\text{Cd}-\text{O}(2)$	2.434(5)	$\text{N}(9)-\text{Cd}-\text{N}(3)$	83.59(17)
$\text{Cd}-\text{N}(3)$	2.526(5)	$\text{N}(4)-\text{Cd}-\text{N}(10)$	88.82(17)
$\text{Cd}-\text{N}(10)$	2.545(5)	$\text{N}(9)-\text{Cd}-\text{N}(10)$	66.84(17)
$\text{Cd}-\text{O}(4)$	2.691(5)	$\text{O}(4)-\text{Cd}-\text{O}(6)$	50.45(16)

which time the toluene was removed and acetone (5  $\text{cm}^3$ ) was added to the resultant reaction mixture. A precipitate was obtained by further addition of diethyl ether, and this was collected and dried to give a crude 27% yield of  $\text{L}^3$ . This reaction was attempted several times but was successful only once, all other times leading to the formation of dppz as a major product, with  $\text{L}^3$  present as only a very minor component, if formed at all. Although the presence of  $\text{L}^3$  was indicated by  $^1\text{H}$ -NMR and mass spectrometry, the very low yield (typically 5% or less) indicated that this synthetic route was not viable.  $^1\text{H}$ -NMR (in  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ,  $J/\text{Hz}$ ): 8.75 (m, 4H), 8.32 (m, 4H), 7.83 (m, 4H), 7.31 (m, 4H), 6.61 (s, 2H), 2.99 (s, 2H). Mass spec found (calc. for  $\text{C}_{31}\text{H}_{20}\text{N}_8$ ) (ES,  $\text{MH}^+$ ): 504.1799 (504.1805).

**4,4'-Ethane-1,2-diylbis(3,6-dipyridin-2-ylpyridazine).  $\text{L}^4$ .** Dptz (0.5 g, 2.12 mmol) was dissolved in  $\text{CHCl}_3$  (10  $\text{cm}^3$ ) to give a deep red solution. 1,5-Hexadiene (0.06  $\text{cm}^3$ , 0.51 mmol) was added and the reaction mixture heated under reflux for 2 d with the solution gradually turning yellow. The solution was left to cool to room temperature and [bis(trifluoroacetoxy)iodo]benzene (0.5 g, 1.18 mmol) was added and the solution stirred for 1 h, during which time it turned black. The solvent was removed and acetone (10  $\text{cm}^3$ ) added to afford a precipitate, which was collected, washed with acetone and dried to give a pale yellow powder (yield 108 mg, 43%). Crystals of  $\text{L}^4 \cdot 2\text{DMSO}$  were grown from deuterated DMSO over a period of a month. Found (calc. for  $\text{C}_{30}\text{H}_{22}\text{N}_8$ ) (%): C 72.37 (72.86), H 4.49 (4.48), N 22.59 (22.66).  $^1\text{H}$ -NMR (in  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ,  $J/\text{Hz}$ ): 8.78–8.72 (m, 6H), 8.56 (s, 2H), 8.12 (dt, 2H,  $J = 7.9$ ,  $J = 1.0$ ), 7.92 (td, 2H,  $J = 7.8$ ,  $J = 2.0$ ), 7.84 (td, 2H,  $J = 7.7$ ,  $J = 1.8$ ), 7.43 (m, 2H,  $J = 7.6$ ,  $J = 4.8$ ,  $J = 1.3$ ), 7.31 (m, 2H,  $J = 7.6$ ,  $J = 4.8$ ,  $J = 1.2$ ), 3.60 (s, 4H).  $^{13}\text{C}$ -NMR (in  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 158.56, 157.30, 155.98, 153.41, 149.42, 148.62, 141.34, 137.30, 137.00, 126.47, 124.78, 124.77, 123.71, 121.80,



33.26. IR  $\nu/\text{cm}^{-1}$ : 3458m, 3064w, 1789w, 1763w, 1580s, 1475s, 1384s, 1259w, 1150w, 1092m, 1080w, 1051w, 992m, 931w, 896w, 836m, 825w, 817w, 791s, 775w, 762m, 747m, 726m, 650s, 620m, 542w, 527w, 406m. Mass spec found (calc. For  $\text{C}_{30}\text{H}_{22}\text{N}_8$ ) (ES,  $\text{MH}^+$ ): 495.2042 (495.2040).

**1,4,6,9-Tetrapyridin-2-ylpyridazino[4,5-g]phthalazine.  $\text{L}^5$ .** To a solution of dptz (0.5 g, 2.12 mmol) in  $\text{CHCl}_3$  ( $10\text{ cm}^3$ ) was added 1,4-cyclohexadiene ( $0.05\text{ cm}^3$ , 0.53 mmol). The solution was heated under reflux for 3 days with a small amount of grey precipitate being formed. The solution was left to cool to room temperature and [bis(trifluoroacetoxy)iodo]benzene (0.5 g, 1.18 mmol) was added. The solution was stirred for a further 1 h, during which time the solution turned black. Aqueous 1 M NaOH ( $10\text{ cm}^3$ ) was added and the  $\text{CHCl}_3$  phase separated. The  $\text{CHCl}_3$  was removed by evaporation and acetone ( $5\text{ cm}^3$ ) added to afford a yellow precipitate which was collected, washed with acetone and dried. The product was purified by re-precipitation from  $\text{CHCl}_3$  by addition of acetone to give a yellow powder (yield 5 mg, 1.9%). Found (calc. for  $\text{C}_{30}\text{H}_{18}\text{N}_8 \cdot 0.5\text{CHCl}_3$ ) (%): C 66.25 (66.58), H 3.24 (3.39), N 20.03 (20.37).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ,  $J/\text{Hz}$ ): 11.01 (s, 2H), 8.86 (m, 4H,  $J = 4.8$ ,  $J = 0.9$ ), 8.48 (m, 4H,  $J = 7.9$ ), 8.04 (m, 4H,  $J = 7.8$ ,  $J = 1.8$ ), 7.55 (m, 4H,  $J = 7.6$ ,  $J = 4.8$ ,  $J = 1.1$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 157.03, 155.41, 148.63, 137.50, 130.15, 126.16, 126.01, 124.60. IR  $\nu/\text{cm}^{-1}$ : 1656m, 1632m, 1384s, 993w, 902w, 836w, 792w, 678w, 652w. Mass spec found (calc. For  $\text{C}_{30}\text{H}_{18}\text{N}_8$ ) (ES,  $\text{MH}^+$ ): 491.1728 (491.1727).

**(11Z)-5,6,11,12,15,16-Hexahydro-1,4,7,10-tetrapyridin-2-yl-cyclododeca[1,2-d:5,6-d']dipyridazine.  $\text{L}^6$ .** To a solution of dptz (0.5 g, 2.12 mmol) in  $\text{CHCl}_3$  ( $10\text{ cm}^3$ ) was added *trans,trans,cis*-1,5,9-cyclododecatriene ( $0.05\text{ cm}^3$ , 0.27 mmol). The solution was heated under reflux for 3 d over which period the solution turned orange. After the solution had been left to cool to room temperature, [bis(trifluoroacetoxy)iodo]benzene (0.5 g, 1.18 mmol) was added and the solution was refluxed for a further 20 min to yield a black reaction mixture. The solvent was removed by evaporation and the crude product was purified by column chromatography (silica-gel 60, 15 cm column, 3 cm diameter) first using MeCN as eluent and collecting  $12 \times 15\text{ cm}^3$  aliquots. The eluent was then changed to acetone, and 20 further aliquots were collected and finally the eluent was changed to methanol. The product crystallised out as white needles from the aliquots collected when acetone was used as eluent. The product was collected, washed with a small quantity of acetone and dried to give colourless crystalline needles, (yield 38 mg, 24.5%). Found (calc. for  $\text{C}_{36.8}\text{H}_{33.2}\text{N}_{8.8} \cdot 0.8(\text{MeOH})$ ) (%): C 73.65 (73.63), H 5.06 (5.57), N 19.04 (18.67).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ,  $J/\text{Hz}$ ): 8.74 (dq, 2H,  $J = 4.8$ ,  $J = 0.8$ ), 8.27 (dq, 2H,  $J = 4.8$ ,  $J = 0.8$ ), 8.00–7.85 (m, 6H), 7.76 (td, 2H,  $J = 7.6$ ,  $J = 1.8$ ), 7.42 (ddd, 2H,  $J = 7.4$ ,  $J = 4.8$ ,  $J = 1.4$ ), 7.23 (ddd, 2H,  $J = 7.5$ ,  $J = 4.8$ ,  $J = 1.3$ ), 5.70 (t, 2H,  $J = 5.3$ ), 3.58 (t, 4H), 3.41 (broad s, 4H), 2.36 (broad s, 4H).  $^{13}\text{C-NMR}$  (in  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 159.10, 158.97, 156.61, 156.53, 148.65, 148.31, 145.14, 139.98, 138.94, 137.01, 136.91, 131.04, 125.07, 124.97, 123.65, 123.50, 28.09, 27.83. IR  $\nu/\text{cm}^{-1}$ : 3458w, 3061w, 3009w, 1763w, 1637w, 1586m, 1568m, 1537w, 1475m, 1383s, 1154w, 1107m, 1053w,

994m, 901w, 836m, 826m, 793m, 746m, 726m, 711m, 677m, 623w, 615m, 517w. Mass spec found (calc. For  $\text{C}_{36}\text{H}_{30}\text{N}_8$ ) (ES,  $\text{MH}^+$ ): 575.2669 (575.2666).

**5,6,11,12,17,18-Hexahydro-1,4,7,10,13,16-hexapyridin-2-yl-cyclododeca[1,2-d:5,6-d':9,10-d'']tripyrizidine.  $\text{L}^7$ .** To a solution of dptz (0.5 g, 2.12 mmol) in  $\text{CHCl}_3$  ( $10\text{ cm}^3$ ) was added *trans,trans,trans*-1,5,9-cyclododecatriene (50 mg, 0.31 mmol) and the red solution heated under reflux for 5 d. The solution maintained its red colour. The solution was cooled to room temperature, [bis(trifluoroacetoxy)iodo]benzene (0.5 g, 1.18 mmol) was added and the solution refluxed for a further 15 min during which time the solution turned black. The reaction solvent was evaporated and the product was purified by column chromatography (silica-gel 60, 15 cm column, 3 cm diameter). Initially, toluene–acetone 2 : 1 was used as eluent but when no further material emerged from the column the eluent was changed to MeOH. The product eluted as the final fraction out of the column to give colourless crystals (yield 0.4%). Found (calc. for  $\text{C}_{48}\text{H}_{36}\text{N}_{12}$ ) (%):  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ,  $\delta/\text{ppm}$ ,  $J/\text{Hz}$ ): 8.25 (m, 6H), 7.87 (td, 6H,  $J = 7.8$ ,  $J = 1.5$ ), 7.64 (d, 6H,  $J = 7.8$ ), 7.40 (td, 6H,  $J = 6.2$ ,  $J = 1.8$ ), 3.47 (s, 12H). Mass spec found (calc. For  $\text{C}_{48}\text{H}_{36}\text{N}_{12}$ ) (ES,  $\text{MH}^+$ ): 781.3265 (781.3259).

#### Complexation reactions

**$[\text{Cu}_4(\text{L}^1)(\text{NO}_3)_6(\text{MeO})_2(\text{MeOH})_2]$  1.**  $\text{L}^1$  (10 mg, 0.02 mmol) dissolved in  $\text{CHCl}_3$  ( $4\text{ cm}^3$ ) was carefully layered over a solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in MeOH ( $4\text{ cm}^3$ ) and the solutions allowed to mix slowly. After one week, green platy crystals suitable for X-ray diffraction were formed. Found (calc. for  $\text{C}_{38}\text{H}_{36}\text{Cu}_4\text{N}_{14}\text{O}_{22}$ ) (%): C 35.35 (35.24), H 2.72 (2.78), N 15.07 (15.15). IR  $\nu/\text{cm}^{-1}$ : 3485s (br), 1656w, 1633w, 1602w, 1383s (br), 1258w, 1163w, 1132w, 1045w, 1021m, 934w, 862w, 835m, 825w, 791m, 751w, 720w, 666w, 648w, 624w.

**$[\text{Cu}_4(\text{L}^1)(\text{NO}_3)_6(\text{MeO})_2(\text{EtOH})_2]$  2.** This was prepared in a similar manner to **1** but in the presence of sodium trimesate (11 mg, 0.04 mmol) dissolved in EtOH ( $4\text{ cm}^3$ ). After one week, a small number of green blocky crystals suitable for X-ray diffraction had formed. Powder X-ray diffraction patterns for bulk **1** and **2** were not consistent with the single crystal structure obtained: we attribute this to the visually apparent loss of crystallinity, and hence structural integrity, which occurs as a result of rapid loss of solvent from the crystals.

**$[\text{Cd}_2(\text{L}^2)(\text{NO}_3)_4(\text{EtOH})_3]$  3.**  $\text{L}^2$  (5 mg, 0.01 mmol) and 4,4'-bipyridine (5 mg, 0.03 mmol) were dissolved in EtOH ( $10\text{ cm}^3$ ), and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (12 mg, 0.04 mmol) was dissolved in EtOH ( $10\text{ cm}^3$ ). The two solutions were allowed to slowly diffuse together to afford colourless acicular crystals suitable for X-ray diffraction. Found (calc. for  $\text{C}_{38}\text{H}_{42}\text{Cd}_2\text{N}_{12}\text{O}_{15}$ ) (%): C 40.26 (40.33), H 3.69 (3.71), N 14.74 (14.86). IR  $\nu/\text{cm}^{-1}$ : 3401s (br), 1639w, 1593w, 1570w, 1384s (br), 1155w, 1117 w, 1032 w, 1007w, 836w, 817w, 785w, 745m, 628w, 623w.

**$[\text{Cd}_2(\text{L}^5)_3(\text{NO}_3)_4]$  4.**  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (12 mg, 0.04 mmol) was dissolved in MeOH ( $4\text{ cm}^3$ ) and carefully layered over a solution of  $\text{L}^5$  (5 mg, 0.01 mmol) in  $\text{CHCl}_3$  ( $4\text{ cm}^3$ ). The

**Table 3** Crystallographic data summary for  $L^1$ ,  $L^1 \cdot 4CHCl_3$ ,  $L^2$ ,  $L^4$  and **1–4**

Compound	$L^1$	$L^1 \cdot 4CHCl_3$	$L^2$	$L^4$	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Formula	$C_{34}H_{22}N_8$	$C_{38}H_{26}Cl_{12}N_8$	$C_{33}H_{25}Cl_3N_8$	$C_{34}H_{34}N_8O_2S_2$	$C_{39.75}H_{37.25}Cl_{3.75}Cu_4N_{14}O_{22.50}$	$C_{41.2}H_{41.2}Cl_{3.6}Cu_4N_{14}O_{22}$	$C_{38}H_{42}Cd_2N_{12}O_{15}$	$C_{30}H_{54}Cd_2N_{28}O_{12}$
<i>M</i>	542.60	1020.07	639.96	650.81	1458.18	1467.46	1131.64	1944.41
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
<i>a</i> /Å	6.0136(17)	6.2391(4)	24.367(6)	18.067(2)	10.403(2)	8.430(2)	9.4936(19)	10.7406(4)
<i>b</i> /Å	29.216(8)	11.6260(8)	5.9124(15)	5.5010(6)	16.763(3)	10.588(3)	10.691(2)	21.5613(10)
<i>c</i> /Å	7.6563(21)	15.4933(11)	21.707(6)	16.801(2)	17.194(3)	16.580(4)	22.746(5)	16.7294(8)
<i>a</i> /°	90	93.237(1)	90	90	80.373(3)	85.393(4)	85.21(3)	90
<i>β</i> /°	91.536(6)	91.763(1)	112.744(4)	102.921(2)	82.560(3)	81.475(4)	85.11(3)	99.066(3)
<i>γ</i> /°	90	100.927(1)	90	90	82.475(3)	84.808(4)	74.06(3)	90
<i>U</i> /Å <sup>3</sup>	1344.7(6)	1100.70(13)	2884.1(13)	1627.5(3)	2912.9(9)	1454.2(7)	2207.5(8)	3825.8(3)
<i>Z</i>	2	1	4	2	2	1	2	2
<i>D<sub>c</sub></i> /g cm <sup>−3</sup>	1.340	1.539	1.474	1.328	1.663	1.676	1.703	1.688
<i>μ</i> (Mo-K $\alpha$ )/mm <sup>−1</sup>	0.08	0.795	0.359	0.209	1.699	1.696	1.046	0.647
<i>F</i> (000)	564	514	1320	684	1467	740	1140	1964
<i>T</i> (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	120(2)
Total reflections	7907	12 506	17 206	9879	33 424	16 426	17 495	39 190
Unique reflections	3390	6702	3307	3702	11 774	8643	12 307	9012
<i>R</i> <sub>int</sub>	0.062	0.017	0.1321	0.062	0.0471	0.060	0.0178	0.141
Observed reflections with <i>I</i> ≥ 2σ( <i>I</i> )	1382	5837	1784	2717	7094	4308	10 190	8770
Final <i>R</i> <sub>1</sub>	0.0458	0.058	0.0571	0.0626	0.0625	0.0842	0.0335	0.0805
w <i>R</i> <sub>2</sub> (all data)	0.1466	0.1454	0.1412	0.1459	0.2130	0.261	0.0863	0.168

solutions were allowed to mix slowly over a period of a week, producing a small number of acicular orange crystals suitable for X-ray diffraction. The amount of material recovered was insufficient for elemental analysis or further characterisation.

### X-Ray crystallographic studies

Single crystal X-ray data collections were performed in Nottingham on Bruker SMART1000 ( $L^1$ ,  $L^2$ ) or Bruker SMART APEX ( $L^4$ , 2DMSO) CCD area detector diffractometers. Those for ( $L^1 \cdot 4CHCl_3$ ), **1**, **2**, and **3** were carried out on a Bruker APEXII instrument at Station 9.8 or 16.2smx at CCLRC Daresbury Laboratory, using wavelengths of 0.6768, 0.6768, 0.6906 and 0.6749 Å, respectively. All instruments were equipped with Oxford Cryosystems open flow cryostats.<sup>19</sup> The data for **4** were collected on a Nonius KappaCCD area detector diffractometer also equipped with an Oxford Cryosystems open flow cryostat,<sup>19</sup> controlled by the COLLECT<sup>20</sup> software package and collected images were processed using DENZO.<sup>21</sup> Structures were solved by direct methods using SHELXS97<sup>22</sup> and full-matrix least squares refinement employed SHELXL97.<sup>23</sup> All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model with  $U_{iso}(H) = 1.2U_{eq}(C)$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. Disorder was encountered in solvent molecules in **1** and **2**. In the case of **1**,  $CHCl_3$  molecules were refined with partial occupancies of 0.75 and 0.5. The refinement model for **2** included one nitrate anion disordered over three positions, with atom O5 modelled over three positions. Atoms O5A, O5B and O5C were refined isotropically with occupancies of 0.40, 0.40 and 0.20, respectively. Similarity restraints were applied to the relevant N...O distances. After refinement, the occupancy of the chloroform solvent molecule was fixed at 0.60. In the case of **3** one EtOH molecule was found to be disordered over two positions, O1–C38–C37 and O1–C38'–C37'. Similarity restraints were applied to the C...O distances, and the occupancies refined to be 0.724(9) and 0.276(9), respectively. In the case of the crystal structure of  $L^2$ , the carbon atom (C17) in the solvate  $CHCl_3$  molecule was found to be disordered over two sites of equal occupancy with shared Cl atoms. Similarity restraints were applied to the C...Cl distances. Other details of crystal data and structure determination are given in Table 3.†

### Acknowledgements

We thank EPSRC and the University of Nottingham for support. We are grateful to CCLRC for access to Station 9.8/16.2smx on the Daresbury SRS and to Dr J. E. Warren and Dr T. J. Prior for experimental advice. We acknowledge the use of the EPSRC National Service for Crystallography at the University of Southampton. MS gratefully acknowledges receipt of a Royal Society Wolfson Merit Award and of a Royal Society Leverhulme Trust Senior Research Fellowship.

† CCDC reference numbers 619843–619850. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611561f

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