Multi-domain hydrogen-bond forming metal chelates: X-ray crystal structures of dicyclopalladated 2,3-bis[6-(2-amino-4-phenylamino-1,3,5-triazinyl)]pyrazine (H_2L) [Pd_2Br_2L] and 2,6-bis[6-(2-amino-4-phenylamino-1,3,5-triazinylium)]-pyridine dichloride

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Two new multi-domain α-diimine ligands capable of tri-hydrogen-bonding interactions are described; the non-planar dicyclopalladated complex [Pd_2Br_2L] 3a (X = Br) has imposed chirality and contains a short non-bonded 1,6-*N*···*N′* contact of 2.75 Å; the cationic (2a) form of the pseudo-terpyridine molecule 2 has a virtually planar central core and is shown to be a potential host material.

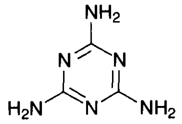
Molecular recognition and self-assembly represent two important strands in modern chemistry.[1] Strategically placed hydrogen-bonding sites which have the potential to enter into complementary interactions are a key feature of one of the design strategies which has emerged in these areas. Specifically, tri-hydrogen-bonding interactions have been utilised for molecular recognition,[2] assembly of molecular monolayers[3] and the formation of mesophases[4] and supramolecular aggregates.[5] Whitesides and coworkers[6] have exploited the tri-hydrogen-bonding capability of melamine (2,4,6-triamino-1,3,5-triazine, **1**) and its derivatives for some elegant crystal engineering. In this communication we describe the linking of two 2,4-diamino-1,3,5-triazinyl moieties by pyridine (**2**) and pyrazine (**3**) spacers which provide alternative domains which may be used either to coordinate metal ions or, in their cationic forms, bind anions, whilst retaining some of the tri-hydrogen-bonding capabilities of melamine.

2,6-Bis[6-(2-amino-4-phenylamino-1,3,5-triazinyl)]pyridine **2** was synthesised from pyridine-2,6-dicarboxylate dimethyl ester and 1-phenylbiguanide and isolated as the bis(triazinylium)pyridine dichloride salt **2a**·Cl_2 in high yield. 2,3-Bis-[6-(2-amino-4-phenylamino-1,3,5-triazinyl)]pyrazine (H_2L, **3**) was isolated in 15% yield by refluxing a mixture of pyrazine-2,3-dicarboxamide, 1-phenylbiguanide and $KOBu^t$ (1 : 2 : 2 molar ratio). Both **2** and **3** have been characterised by spectroscopic and microanalytical techniques.†

Compounds **2** and **3** have quite different molecular recognition possibilities. **2** has a central tridentate (*N,N′,N″*) ligand moiety with two adjacent NH_2 groups, whereas **3** has three potential bidentate (*N,N′*) coordination sites, only one of which has adjacent NH_2 groups. The recognition capabilities of **2** and **3**, clearly, may also be modified by protonation.

The X-ray structural analysis of the diprotonated form of **2** (**2a**·Cl_2) reveals that protonation has occurred on the triazine nitrogen atoms within the central cavity. The structure‡ (Fig. 1), shows the three *N*-heterocyclic rings in this pyridyl derivative to be essentially coplanar with dihedral angles between these rings in the range 0.3–1.5°. This conformation is stabilised *via* four N–H···Cl hydrogen bonds [3.10–3.30 Å] to one of the chloride anions, Cl(1). Symmetry related molecules are linked *via* N–H···Cl hydrogen bonds between each of the remaining amino N–H groups, N(7) and N(28), and Cl(2) (3.27 and 3.28 Å) to form zigzag chains that extend in the crystallographic *b* direction, as shown in Fig. 2.

The four inwardly directed N–H bonds together with the nitrogen atom N(16) of the central pyridyl ring (Fig. 1) form a cleft-like recognition site.[7] For example, the pseudo-guanidinium moieties N(14)–C(12)–N(11)N(13) and N(27)–C(25)–N(26)N(24) may have the appropriate structural characteristics



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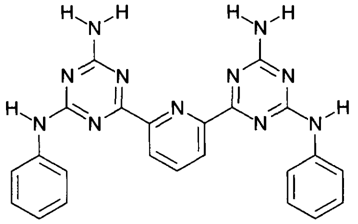

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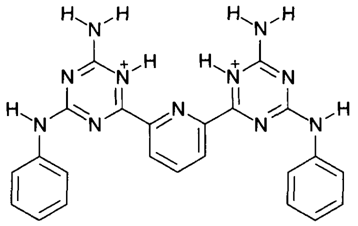
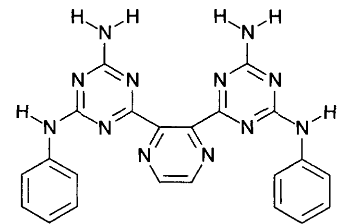


2a



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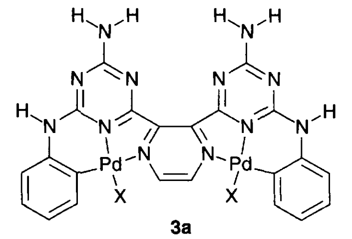

3a

(X = Cl or Br)

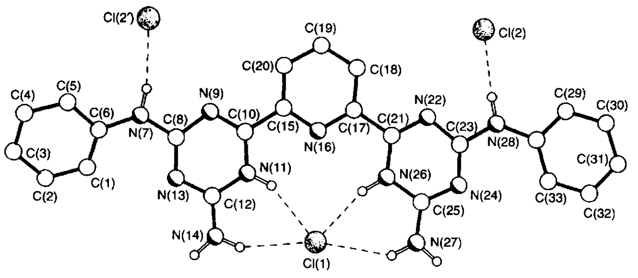

Fig. 1 Molecular structure of 2,6-bis[6-(2-amino-4-phenylamino-1,3,5-triazinylium)]pyridine dichloride **2a**. N–H···Cl hydrogen bonding geometries: N(11)···Cl(1) 3.16, H···Cl(1) 2.33 Å, N–H···Cl 153°; N(14)···Cl(1) 3.30, H···Cl(1) 2.48Å, N–H···Cl 152°; N(26)···Cl(1) 3.10, H···Cl(1) 2.23 Å, N–H···Cl 163°; N(27)···Cl(1) 3.26, H···Cl(1) 2.51 Å, N–H···Cl 141°; N(7)···Cl(2) 3.27, H···Cl(2) 2.40 Å, N–H···Cl 162°; N(28)···Cl(2) 3.28, H···Cl(2) 2.38 Å, N–H···Cl 172°.

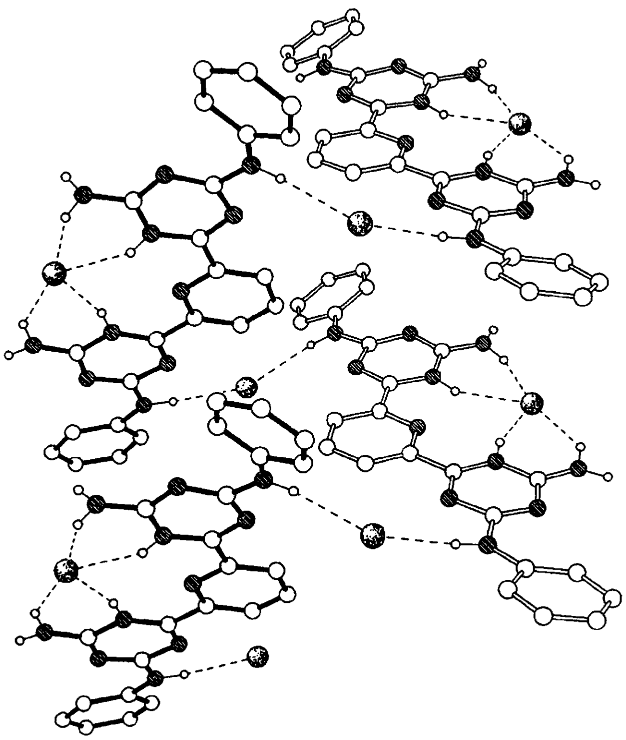

Fig. 2 Part of one of the N–H···Cl hydrogen-bonded zigzag chains present in the structure of **2a**·Cl_2

for the recognition of carbonate, phosphate or sulfonate anions.[8]

When compound **3** (H_2L) is reacted with $Na_2[PdCl_4]$ (1 : 2 molar ratio) in acetone–water (7 : 10, v/v), the dicyclometallated compound $[Pd_2Cl_2L]$ **3a** (X = Cl) is obtained.† The X-ray structural analysis of the corresponding bromo-compound,‡ shown in Fig. 3 [prepared by the reaction of **3a** (X = Cl) with lithium bromide in dimethyl sulfoxide] shows the coordination geometries of the two independent square-planar palladium ions to be equivalent within statistical significance, and also very similar to that observed in the closely related complex [PdClL′] [HL′ = 2-amino-4-phenylamino-6-(2-pyridyl)-1,3,5-triazine].[9] Although the two palladium inner coordination spheres are essentially planar (maximum deviation 0.05 Å), in each case the three coordinated six-membered rings are non-coplanar and are arranged helically with respect to their parent metal centre. This helicity, coupled with a pronounced twisting of the central pyrazine ring about its *N*···*N*′ axis [the C(15)···C(17) and C(20)···C(18) vectors are inclined by 7°], results in both an overall propeller-like conformation for the complex as a whole and an imposed chirality.§ Associated with this geometry are torsional twists about the C(10)–C(15), C(15)–C(20) and C(20)–C(21) bonds of 18, 20 and 21°, a noticeably short 1,6-*N*···*N*′ non-bonded contact of 2.75 Å between N(11) and N(22) and a resultant 24° dihedral angle between the two inner coordination spheres. This twist-conformation is reminiscent of strained 1,1′-binaphthyl derivatives such as (*P*)-7-phenyldinaphtho[2,1-*b*;1′,2′-*d*)]phosphole (torsion angle between two naphthyl planes 29°)[10] and $[Ru(bpy)_2(1,1'\text{-bisisoquinoline})]^{2+}$,[11] and the resultant chirality suggests the possibility for the selective enantiomeric binding of molecules with complementary hydrogen-bonding groups.

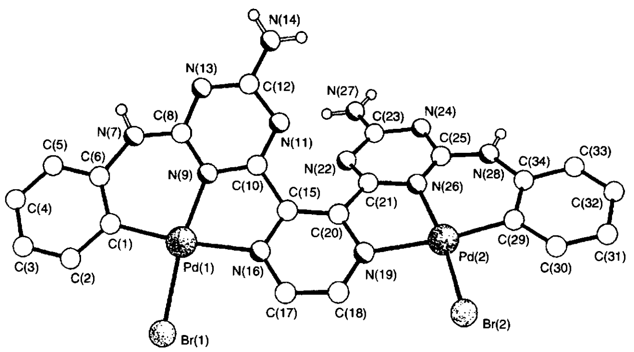

Fig. 3 Molecular structure of $[Pd_2Br_2L]$ **3a**, (X = Br) with atomic numberings. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.004(12), Pd(2)–C(29) 1.992(11), Pd(1)–N(9) 2.000(9), Pd(2)–N(26) 2.009(9), Pd(1)–N(16) 2.137(9), Pd(2)–N(19) 2.141(9), Pd(1)–Br(1) 2.416(2), Pd(2)–Br(2) 2.413(2), C(1)–Pd(1)–N(9) 92.6(4), C(29)–Pd(2)–N(26) 92.6(4), N(9)–Pd(1)–N(16) 79.4(3), N(26)–Pd(2)–N(19) 79.3(3), N(16)–Pd(1)–Br(1) 92.4(2), N(19)–Pd(2)–Br(2) 92.0(2), Br(1)–Pd(1)–C(1) 95.5(3), Br(2)–Pd(2)–C(29) 96.0(4), C(6)–N(7)–C(8) 130.8(10), C(25)–N(28)–C(34) 130.4(10).

The only notable intermolecular interactions are (*i*) an N–H···Br hydrogen-bond [N(14)···Br(1′) 3.49 Å] which produces a polar chain that extends along the crystallographic *a* direction and (*ii*) the Pd atoms of adjacent chains of opposite chirality are positioned almost directly above their symmetry related counterparts at distances of 3.40 Å [Pd(1)] and 3.46 Å [Pd(2)], as shown in Fig. 4. Accompanying this off-set stacked motif, there are favourable π–π interactions between a pyrazine ring in one chain and a phenyl ring in another, and *vice versa.* These combined interactions result in corrugated sheets of molecules that extend in the crystallographic *a* and *b* directions.

We have thus demonstrated that 2,4-diamino-1,3,5-triazinyl moieties may be linked through heterocyclic spacer molecules to yield molecules with potentially interesting molecular recognition properties. Besides retaining some of the useful trihydrogen-bonding capabilities of the parent melamine molecule, these novel species are also able to incorporate anions and metal ions in clefts created by the incorporation of the heterocyclic spacer molecules.

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Footnotes

† Numberings for ^{1}H NMR are in accord with those for crystallographic results. Characterisation of **2** (found: C, 60.80; H, 4.40; N, 32.55; $C_{23}H_{19}N_{11}\cdot H_2O$ requires C, 59.10; H, 4.55; N, 32.95%), mp 336 °C (decomp.). ^{1}H NMR [$(CD_3)_2SO$]: δ 9.7 (2 H, br s, NH), 8.6–6.5 (4 H, v br, NH_2). 8.50 (1 H, d, H^{19}), 8.20 (2 H, t, H^{18} and H^{20}), 7.83 (4 H, d, H^1, H^5, H^{29} and H^{33}), 7.35 (4 H, t, H^2, H^4, H^{30} and H^{32}), 7.05 (2 H, t, H^3 and H^{31}).

2a·Cl_2 (found: C, 50.20; H, 4.75; N, 26.55; $C_{22}H_{19}N_{11}\cdot 2H_2O\cdot 2HCl$ requires C, 49.50; H, 4.50; N, 27.60%), mp 330 °C. ^{1}H NMR [$(CD_3)_2SO$]: δ 13.5 (1 H, br s, NH), 11.5–11.0 (1 H, br s, NH), 9.7–9.3 (1 H, br s, NH), 8.3–8.1 (1 H, br s, NH), 7.7 (1 H, br s, NH), 8.7–8.5 (3 H, br, H^{18}, H^{19} and

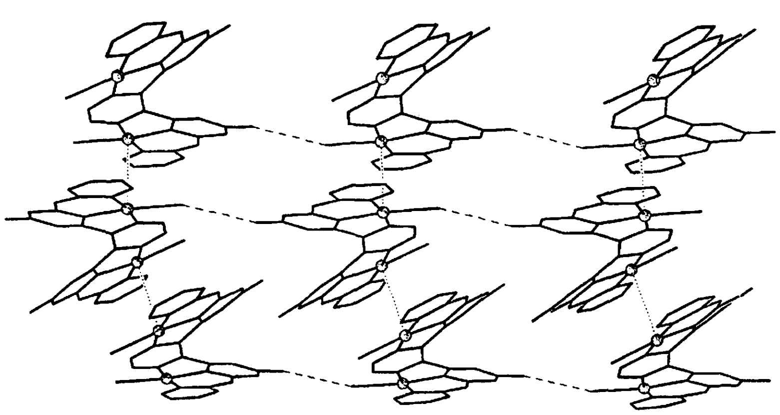

Fig. 4 A portion of a corrugated sheet in the packing of **3a** (X = Br), showing both the N–H···Br hydrogen bonding and the close Pd···Pd approaches

H^{20}), 7.86 (4 H, d, H^{1}, H^{5}, H^{29} and H^{33}), 7.46 (4 H, t, H^{2}, H^{4}, H^{30} and H^{32}), 7.25 (2 H, t, H^{3} and H^{31}). MS (FAB): *m/z* 450 (M + H, 100%).

3 (found: C, 56.52; H, 4.29; N, 35.14. $C_{22}H_{18}N_{12}{\cdot}H_2O$ requires C, 56.40; H, 4.30; N, 35.88%). ^{1}H NMR [$(CD_3)_2SO$]: δ 9.5 (2 H, br s, NH), 8.85 (2 H, s, H^{17} and H^{18}), 7.6 (4 H, br s, H^{1}, H^{5}, H^{29} and H^{33}), 7.3 and 7.12 (4 H, br s, NH_2), 7.25 (4 H, t, H^{2}, H^{4}, H^{30} and H^{32}), 6.80 (2 H, t, H^{3} and H^{31}).

3a (X = Cl) [found: C, 34.70; H, 2.95; N, 19.10; $C_{22}H_{16}Cl_2N_{12}Pd_2{\cdot}H_2O{\cdot}(CH_3)_2SO$ requires C, 34.80; H, 2.90; N, 20.30%]. ^{1}H NMR [$(CD_3)_2SO$]: δ 10.80 (2 H, s, NH), 9.35 (2 H, s, H^{17} and H^{18}), 8.01 (2 H, s, NH_2), 8.01 (2 H, d, H^{2} and H^{30}), 7.81 (2 H, s, NH_2), 7.10 (2 H, d, H^{5} and H^{33}), 7.01 (2 H, t, H^{4} and H^{32}), 6.70 (2 H, t, H^{3} and H^{31}).

‡ Suitable crystals of **2a**·Cl_2 were obtained as a methanol solvate by the slow diffusion of diethyl ether into a methanolic solution of the compound. *Crystal data*: $C_{23}H_{21}Cl_2N_{11}{\cdot}2CH_3OH$, M = 586.5, monoclinic, space group $P2_1/c$, a = 17.894(5), b = 8.293(2), c = 19.596(8) Å, β = 95.15(3)°, U = 2896(2) Å^3, Z = 4, D_c = 1.34 g cm^{-3}, μ(Cu-Kα) = 23.8 cm^{-1}, $F(000)$ = 1224. A yellow needle of dimensions 0.24 × 0.14 × 0.07 mm was used. Data were measured on a Siemens P4/RA diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and all the non-hydrogen atoms of the cation, anions and the major occupancy solvent molecules were refined anisotropically using full-matrix least squares to give $R1$ = 0.075, $wR2$ = 0.167 for 1992 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$] and 386 parameters.

Suitable crystals of **3a**, (X = Br) were obtained as a mixed dimethylsulfoxide–methanol solvate by the slow diffusion of dichloromethane into a dimethylsulfoxide solution of the compound. *Crystal data*: $C_{22}H_{16}Br_2N_{12}Pd_2{\cdot}3(CH_3)_2SO{\cdot}0.5CH_3OH$, M = 1071.5, monoclinic, space group $P2_1/c$, a = 11.068(1), b = 15.090(2), c = 22.936(2) Å, β = 99.70(1)°, U = 3776(1) Å^3, Z = 4, D_c = 1.89 g cm^{-3}, μ(Mo-Kα) = 32.9 cm^{-1}, $F(000)$ = 2116. A thin red plate of dimensions 0.40 × 0.27 × 0.03 mm was used. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy-atom method and all the non-hydrogen atoms of the complex and the major occupancy Me_2SO solvent molecules were refined anisotropically using full-matrix least squares to give $R1$ = 0.069 $wR2$ = 0.150 for 3729 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$] and 479 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ As the complex crystallises in a centrosymmetric space group it contains equal numbers of right- and left-handed propellers.

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