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Synthesis and crystal structures of silver(I), palladium(II), zinc(II) and cobalt(II) complexes of the ditoptic ligand 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene

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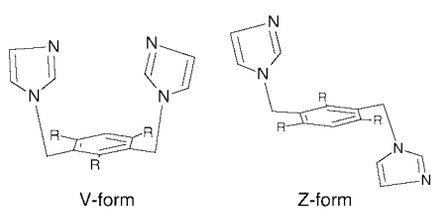
Complexes of 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bitmb) with silver(I), palladium(II), zinc(II) and cobalt(II) salts have been characterized in the solid state by single-crystal X-ray analysis. The topology of the structures in the solid state, namely finite *versus* infinite, is found to dependent on the coordination geometry of the metal atoms. For Ag(I) (linear N_2 geometry) and Pd(II) (square-planar N_4), crystallization with bitmb produces an M_2L_2 cyclic dimer of composition $[Ag_2(bitmb)_2](PF_6)_2\cdot 2CH_3CN$ (**1**) or an M_2L_4 cage complex $[Pd_2(bitmb)_4]Cl_4\cdot 8H_2O\cdot 1.5CH_3CN$ (**2**). For Zn(II) (tetrahedral N_2O_2) or Co(II) (octahedral N_6), crystallization with bitmb produces a 1D zigzag chain network of $[Zn(bitmb)(CH_3CO_2)(C_2H_5OH)](OH)$ (**3**) or an infinite 1D poly-macrocycle chain network $[Co(bitmb)_2(CH_3CN)_2](ClO_4)_2\cdot 2C_2H_5OH$ (**4**). It is also found that the conformations of the bitmb ligand are obviously controlled by the coordination number of the central metal ions. When coordinated with silver(I) (coordination number $n = 2$), palladium(II) ($n = 4$) or zinc(II) ($n = 4$), bitmb shows a *cis*,*cis*-conformation, but in the case of cobalt(II) ($n = 6$), bitmb shows a *trans*,*trans*-conformation. The results also show that the $\pi\cdots\pi$ interactions together with the hydrogen bonds co-affect inorganic supramolecular formation.

Metal-directed assembly has been proven to be a useful methodology in supramolecular chemistry and significant progress has been achieved in this area.[1] Such progress makes it possible to rationally design and synthesise supramolecular complexes with one-, two- or three-dimensional networks. Frameworks with specific topologies such as honeycomb grids and cages have been obtained by assembly of suitable metal ions with rationally designed tripodal ligands,[2–11] such as 1,3,5-tris(benzonitrile) (tcb),[3] 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt),[4] 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb)[8,9] and 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib).[10,11] For example, tcb[3] gives an extended honeycomb framework by assembly with $Ag(O_3SCF_3)$, while for tpt,[4] an M_6L_4 type of cage was obtained by reaction of the ligand with $Pd(en)(NO_3)_2$. Honeycomb frameworks have been obtained by assembly of $Cu(CH_3CO_2)_2$ with tpt[7] or with titmb,[8] and an M_3L_2 cage can also be obtained by assembly of $Pd(en)(NO_3)_2$ with 1,3,5-tris-(4-pyridylmethyl)benzene[4] or assembly of $Zn(CH_3CO_2)_2$ with tib.[10] Recently, a 3D nanoporous framework[11] $[Cu_6(OH)_4(tib)_8]^{8+}$ has been obtained by reaction of $Cu(CH_3CO_2)_2$ with tib in aqueous solution. Thus understanding how these considerations affect metal coordination and influence crystal packing is at the heart of controlling coordination supramolecular arrays. There is growing interest in finding alternative approaches for building new inexpensive and easy-to-prepare supramolecular systems. According to these ideas, we have reported the synthesis and crystal structure of a flexible ditoptic ligand 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bitmb),[12] which is a derivate of titmb[8,9] but lacks an imidazol-1-ylmethyl group. There can be two conformations when bitmb coordinates with metal ions, namely, *cis*,*cis*-conformation (V-form) and *trans*,*trans*-conformation (Z-form) (Scheme 1). An M_3L_4 twin-cage complex[12] was formed with bitmb in V-form.

In order to study the influence of metal ion stereochemical preference on the supramolecular construction and ligand conformation, a study was carry out with monovalent silver(I) salts and bivalent palladium(II), zinc(II) and cobalt(II) with different counter anions, PF_6^-, Cl^-, $CH_3CO_2^-$ and ClO_4^-. Here we report the crystal structures of the bitmb ligand with silver(I) hexafluorophosphate ($AgPF_6$), tetrakis(acetonitrile)dichloropalladium(II) $\{[Pd(CH_3CN)_4]Cl_2\}$, zinc(II) acetate dihydrate ($Zn(CH_3CO_2)_2\cdot 2H_2O$) and cobalt(II) perchlorate hexahydrate ($Co(ClO_4)_2\cdot 6H_2O$). The topology of these structures is found to depend on the coordination geometry of the metal ions, as finite structures are observed with silver(I) or palladium(II) and infinite structures are formed with zinc(II) or cobalt(II). It is also found that the conformations of the bitmb ligand are obviously controlled by the coordination number of the central metal ions, as *cis*,*cis*-conformation is observed with silver(I), palladium(II) or zinc(II) ions, and *trans*,*trans*-conformation is found with cobalt(II) ion.



Scheme 1 bitmb, R = Me

Experimental

General methods

Solvents such as acetonitrile and methanol were dried and purified by distillation before use. Other reagents were commercially available and used as received without further purification. The flexible ditoptic ligand bitmb (bitmb = 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene) was prepared

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according to the literature methods.[12] The C, H and N analyses were performed on a Perkin-Elmer 240C elemental analyzer. 500 MHz ^{1}H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference at room temperature, electrospray mass spectral measurements on a LCQ System (Finngan MAT, USA) using methanol as mobile phase, IR (KBr disk) on a Bruker EQUINOS-55 spectrometer and FAB mass spectral measurements on a VG ZAB-HS in acetonitrile solution.

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Syntheses

$[Ag_2(bitmb)_2](PF_6)_2\cdot 2CH_3CN$ 1. A solution of bitmb (28 mg, 0.1 mmol) in ethanol solution (5 ml) was added to an acetonitrile solution (10 ml) of $AgPF_6$ (26 mg, 0.1 mmol) at room temperature with stirring. Standing the filtrate at room temperature for about a month resulted in colorless crystals, yield 45 mg (83%). Found: C, 38.64; H, 4.07; N, 10.58. Calc. for $C_{34}H_{40}N_8P_2F_{12}Ag_2$: C, 38.29; H, 3.78; N, 10.51%. ^{1}H NMR (CD_3CN, 293 K, ppm): δ 2.27 (s, 6H, CH_3), 2.54 (3H, s, CH_3), 5.39 (4H, s, CH_2), 7.23 (2H, s, H_{im}), 7.57 (2H, s, H_{im}), 7.71 (2H, s, H_{bz}, H_{im}), 7.89 (1H, s, H_{im}). M_{Calc} = 1148.5, FAB-MS: found: *m*/*z* 922, calc for $[M - 2CH_3CN - PF_6]^+$: 921.4. IR (KBr, cm^{-1}): 3149 (m), 2974 (w), 2919 (w), 1605 (w), 1516 (m), 1463 (w), 1398 (w), 1302 (w), 1236 (m), 1146 (m), 1093 (m), 1025 (w), 838 (vs), 749 (m), 686 (w), 654 (m), 620 (w), 558 (s).

$[Pd_2(bitmb)_4]Cl_4\cdot 8H_2O\cdot 1.5CH_3CN$ 2. A solution of bitmb (56 mg, 0.2 mmol) in aqueous acetonitrile solution (1 : 2, 15 ml) was added to an acetonitrile solution (10 ml) of $Pd(CH_3CN)_4Cl_2$ (26 mg, 0.1 mmol) at room temperature with stirring. Standing the filtrate at room temperature for about ten days resulted in colorless crystals, yield 90%. Found: C, 50.15; H, 6.02; N, 14.33. Calc. for $[Pd_2(bitmb)_4]Cl_4\cdot 9H_2O\cdot 1.5CH_3CN$ ($C_{71}H_{102.5}Pd_2Cl_4N_{17.5}O_9$): C, 50.16; H, 6.07; N, 14.41%. ^{1}H NMR (D_2O, 293 K, ppm): δ 1.99 (s, 6H, CH_3), 2.17 (3H, s, CH_3), 5.13 (2H, s, CH_2), 5.26 (2H, s, CH_2), 6.94 (2H, s, H_{im}), 6.99 (2H, s, H_{im}), 7.21 (2H, s, H_{bz}, H_{im}), 7.39 (1H, s, H_{im}). M_{Calc} = 1476.1, ESI-MS: found: *m*/*z* 466.7, calc. for $[M + CH_3OH - 3Cl]^{3+}$: 466.7. IR (KBr, cm^{-1}): 3414 (br s), 3109 (m), 2974 (w), 2920 (w), 1608 (m), 1518 (m), 1453 (w), 1409 (w), 1382 (w), 1311 (w), 1236 (m), 1101 (vs), 1021 (w), 965 (w), 831 (w), 754 (w), 688 (w), 657 (w), 620 (w).

$[Pd_2(bitmb)_4](PF_6)_4\cdot 8H_2O\cdot CH_3CN$ 2′. A solution of bitmb (56 mg, 0.2 mmol) in aqueous acetonitrile solution (1 : 2, 15 ml) was added to an acetonitrile solution (10 ml) of $Pd(CH_3CN)_4Cl_2$ (26 mg, 0.1 mmol) at room temperature with stirring. A solution of NH_4PF_6 (65 mg, 0.4 mmol) in acetonitrile solution (5 ml) was then added to the filtrate at room temperature resulting in colorless microcrystals, yield 90%. Found: C, 40.00; H, 5.02; N, 11.33. Calc. for $[Pd_2(bitmb)_4](PF_6)_4\cdot 8H_2O\cdot CH_3CN$ ($C_{70}H_{99}N_{17}Pd_2P_4O_8F_{24}$): C, 40.05; H, 4.75; N, 11.34%. M_{Calc} = 2099.36, FAB-MS: found: *m*/*z* 1852, calc. for $[M + CH_3CN - 8H_2O - PF_6]^+$: 1851.33; *m*/*z* 1769, calc. for $[M - CH_3CN - 8H_2O - PF_6]^+$: 1769.22; *m*/*z* 1624, calc. for $[M - CH_3CN - 8H_2O - 2PF_6]^{2+}$: 1624.26; *m*/*z* 812, calc. for $[M - CH_3CN - 8H_2O - 3PF_6 - 2L - Pd]^+$: 812.13.

$[Zn(bitmb)(CH_3CO_2)(C_2H_5OH)](OH)$ 3. A solution of bitmb (28 mg, 0.10 mmol) in ethanol (5 ml) was added to an ethanol solution (5 ml) of $Zn(CH_3CO_2)_2\cdot 2H_2O$ (22 mg, 0.10 mmol) at room temperature. The mixture was filtered after stirring for about 1 hour to give a colorless solution. Standing of this filtrate over a period of one week resulted in the formation of colorless rhombic crystals. Yield 50%. Found: C, 52.52; H, 5.40; N, 11.64. Calc. for $[Zn(bitmb)(CH_3CO_2)(C_2H_5OH)](OH)\cdot 2/3H_2O$ ($C_{21}H_{31.33}N_4ZnO_{4.66}$): C, 52.56; H, 6.58; N, 11.68%. IR (KBr, cm^{-1}): 3465 (br s), 3139 (m), 2979 (w), 2925 (m), 1619 (vs), 1590 (vs), 1522 (m), 1475 (w), 1394 (vs), 1328 (m), 1236 (m), 1100 (m), 1087 (s), 1020 (m), 950 (m), 840 (m), 747 (m), 629 (m), 658 (m), 619 (m), 508 (w).

$[Co(bitmb)_2(CH_3CN)_2](ClO_4)_2\cdot 2C_2H_5OH$ 4. A solution of bitmb (56 mg, 0.2 mmol) in acetonitrile (15 ml) was added to an ethanol solution (10 ml) of $Co(ClO_4)_2\cdot 6H_2O$ (37 mg, 0.1 mmol) at room temperature with stirring. Standing the filtrate at room temperature for about two weeks resulted in pale red prism crystals, yield 75%. Found: C, 63.50; H, 7.22; N, 17.63. Calc. for $C_{42}H_{58}CoCl_2N_{10}O_{10}$: C, 63.54; H, 7.36; N, 17.64%. IR (KBr, cm^{-1}): 3436 (br s), 3134 (m), 2979 (w), 2922 (w), 2029 (m), 1629 (m), 1607 (m), 1518 (s), 1456 (m), 1400 (w), 1300 (w), 1229 (s), 1091 (vs), 937 (m), 832 (m), 757 (m), 687 (m), 662 (m), 623 (s).

Crystallography

The intensity data of complexes **1**–**4** were collected on a Bruker CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at room temperature. All absorption corrections were performed using the SADABS program.[13] The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares method against F_o^2 (SHELXL-97).[14] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Details of the crystal parameters, data collection and refinement for complexes **1**–**4** are listed in Table 1, and selected bond distances and angles are given in Table 2.

CCDC reference numbers 154826, 171467, 172860 and 172861.

See http://www.rsc.org/suppdata/dt/b1/b104833n/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and crystal structures of complexes 1–4

The preparation of the complexes **1**–**4** is readily achieved by reaction of silver(I), palladium(II), zinc(II) or cobalt(II) salts with bitmb in the molar ratio of 1 : 1, 1 : 2, 1 : 1 or 1 : 2, respectively. The elemental C, H and N analysis confirmed the chemical formulation for these complexes. The chemical formulation for complexes **1** and **2** were confirmed by the FAB or electrospray mass spectrum, respectively. The M_2L_4 cage complex **2′** is obtained by adding an excess amount of NH_4PF_6 to an aqueous acetonitrile solution containing $Pd(CH_3CN)_4Cl_2$ and bitmb in the molar ratio of 1 : 2, and the formulation $[Pd_2(bitmb)_4](PF_6)_4\cdot 8H_2O\cdot CH_3CN$ is confirmed by elemental analyses and FAB mass spectra. The silver complex **1** is stable to oxygen in both the solid and solution states in the dark. The single crystals of the four complexes effloresce quickly when removed from the mother-liquor.

Fig. 1 shows the single-crystal X-ray structure of **1**, which is a centrosymmetric rectangular-shaped [2 + 2] dimetallo-paracyclophane[15] within which a well-ordered PF_6^- anion is encapsulated, while external to the macrocycle is another PF_6^- anion and two acetonitrile molecules. Each Ag atom is coordinated linearly to two imidazole nitrogen atoms from two bitmb ligands and the bitmb ligand is in a *cis*,*cis*-conformation (V-form) and attaches to two silver(I) atoms with its two imidazolyl arms. The Ag–N distances of 2.112–2.126 Å are within the range of reported values[16] as shown in Table 2. As have been observed in other dimeric silver complexes,[15] the geometry at the silver atom is distorted T-shaped, and the axial site is coordinated by water molecules or nitrate anions. However, it has previously been noted[17] that the absence of axial coordination is rare in such compounds. In this dimer, the two imidazolyl rings of each bitmb are inclined to the phenyl ring at angles of 91.8 and 82.6°, respectively; the dihedral angles of the two imidazole rings of each bitmb and coordinated with the same silver(I) atom are all 41.7°; and the two phenyl rings of the

Table 1 Summary of crystal data and refinement results for complexes **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{38}H_{46}N_{10}P_2F_{12}Ag_2$	$C_{71}H_{100.5}Pd_2Cl_4N_{17.5}O_8$	$C_{21}H_{30}N_4O_4Zn$	$C_{42}H_{58}CoCl_2N_{10}O_{10}$
Formula weight	1148.51	1681.79	466.15	992.822
T/°C	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pnma*	$P\bar{1}$
a/Å	8.799(2)	11.7708(15)	11.960(2)	11.430(2)
b/Å	9.907(2)	14.3618(19)	12.150(2)	11.790(2)
c/Å	13.853(3)	14.4184(19)	15.710(3)	11.820(2)
α/°	98.37(3)	96.710(2)	90	84.90(3)
β/°	101.74(3)	113.302(2)	90	87.80(3)
γ/°	102.62(3)	94.745(2)	90	65.80(3)
U/Å^3	1130.7(4)	2201.0(5)	2282.9(7)	1447.1(4)
Z	2	1	2	1
μ/mm^{-1}	1.028	0.587	0.585	0.433
Measured/independent reflections	6383/4742	12124/6036	2443/1723	5819/3799
R_{int}	0.0474	0.0247	0.0249	0.0244
$R1(I > 2\sigma(I))$	0.0757	0.0680	0.0756	0.0832
$wR2$ $(I > 2\sigma(I))$	0.2062	0.1791	0.2518	0.2510

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**–**4**

$[Ag_2(bitmb)_2](PF_6)_2\cdot 2CH_3CN$ **1**					
Ag1–N1	2.112(6)	Ag1–N5	2.126(5)	N1–Ag1–N5	179.2(2)
Ag1–F3	2.887(7)	Ag1–F1	3.064(8)	Ag2–F4	3.064(8)
Ag2–F6	2.887(7)	P1–F3	1.601(4)	P1–F6	1.601(4)
Ag1 · · · Ag2	7.75				
P1–F4	1.572(5)	P1–F1	1.572(5)	P1–F1–Ag1	109.0(2)
P1–F3–Ag1	116.3(3)	P1–F6–Ag2	116.3(3)	P1–F4–Ag2	109.0(2)
$[Pd_2(bitmb)_4]Cl_4\cdot 8H_2O\cdot 1.5CH_3CN$ **2**					
Pd1–N1	2.004(2)	Pd1–N3	2.005(19)	Pd1–N5	2.017(19)
Pd1–N7	2.009(18)				
N1–Pd1–N7	89.09(8)	N1–Pd1–N3	90.88(8)	N3–Pd1–N5	90.33(8)
N3–Pd1–N7	176.37(8)	N7–Pd1–N5	89.68(8)	N1–Pd1–N5	178.70(8)
$[Zn(bitmb)(CH_3CO_2)(C_2H_5OH)](OH)$ **3**					
Zn1–O1	1.968(6)	Zn1–N1′	2.018(4)	Zn1–O3	2.223(11)
Zn1–N1	2.018(4)	Zn1–O3′	2.223(11)	N1–Zn1–O3	120.9(3)
N1–Zn1–N1′	108.6(2)	O1–Zn1–N1′	111.92(13)	O1–Zn1–O3	102.9(3)
N1′–Zn1–O3	120.9(3)	O1–Zn1–N1	111.92(13)	N1–Zn1–O3′	100.0(3)
N1′–Zn1–O3′	100.0(3)	O1–Zn1–O3′	102.9(3)	O3–Zn1–O3′	24.1(4)
$[Co(bitmb)_2(CH_3CN)_2](ClO_4)_2\cdot 2C_2H_5OH$ **4**					
Co–N2′	2.117(3)	Co–N2	2.117(3)	Co–N7′	2.129(3)
Co–N7	2.129(3)	Co–N4	2.187(4)	Co–N4′	2.187(4)
N2–Co–N7	88.29(13)	N7–Co–N4	90.98(14)	N2–Co–N7′	91.71(13)
N7–Co–N4′	89.02(14)	N2′–Co–N7	91.71(13)	N2–Co–N4	91.50(14)
N2′–Co–N7′	88.29(13)	N2–Co–N4′	88.50(14)	N7–Co–N7′	180.0(3)
N7′–Co–N4	89.02(14)	N2′–Co–N4	88.50(14)	N7′–Co–N4′	90.98(14)
N2′–Co–N4′	91.50(14)	N4–Co–N4′	180.0(3)	N2–Co–N2′	180.00(19)

[a] Symmetry transformations used to generate equivalent atoms: x, y, z; $-x, -y, -z$ for **1**; x, y, z; $-x, -y, -z$ for **2**; x, y, z; $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; $-x, y + \frac{1}{2}, -z$; $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; $-x, -y, -z$; $x - \frac{1}{2}, y, -z - \frac{1}{2}$; $x, -y - \frac{1}{2}, z$; $-x - \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$ for **3**; x, y, z; $-x, -y, -z$ for **4**.

two bitmb ligands are parallel to each other. The dimensions of the dimer are defined by the distance between the centroids of the two phenyl rings of bitmb (11.00 Å) and the intramolecular Ag · · · Ag separation (7.75 Å), and the unit possesses a crystallographic symmetry center *i* located at the P atom of the PF_6^- anion enclosed inside the cavity. A PF_6^- anion is encapsulated in this rectangular-shaped dimer, although PF_6^- ions normally act as non-coordinated anions.[18,19] The encapsulated anion within the dimeric **1** makes weak contacts with the silver centers (Ag1–F1 3.064, Ag1–F3 2.887, Ag2–F4 3.064, Ag2–F6 2.887 Å, indicated by dashed lines in Fig. 1(a)) which are a little larger than corresponding Ag–F bonds found in the literature.[18] It is a challenge using simple species to capture anionic[20] or molecular guests. Some anionic encapsulation compounds have been reported containing triflate,[21] chloride[22] and nitrate[19] but for M_2L_2 dimers, reports are rare. There are two types of intermolecular π · · · π interactions formed between the phenyl rings of nearest neighboring dimers, as shown in Fig. 1(b) and (c). The π · · · π interactions formed in a face-to-face orientation are denoted as type A with a center-to-center distance of 3.51 Å, while that formed in a back-to-back orientation is denoted type B with a center-to-center distance of 3.70 Å. Each dimer makes four π · · · π interactions with four adjacent dimers, the overall packing arrangement forming a two-dimensional brick-wall structure *via* two types of π · · · π interactions in the *ab* plane (Fig. 1(c)). The packing diagram of the two-dimensional brick-wall along the *a* axis as shown in Fig. 1(d) reveals that large void spaces have been formed between 2D networks in which the non-

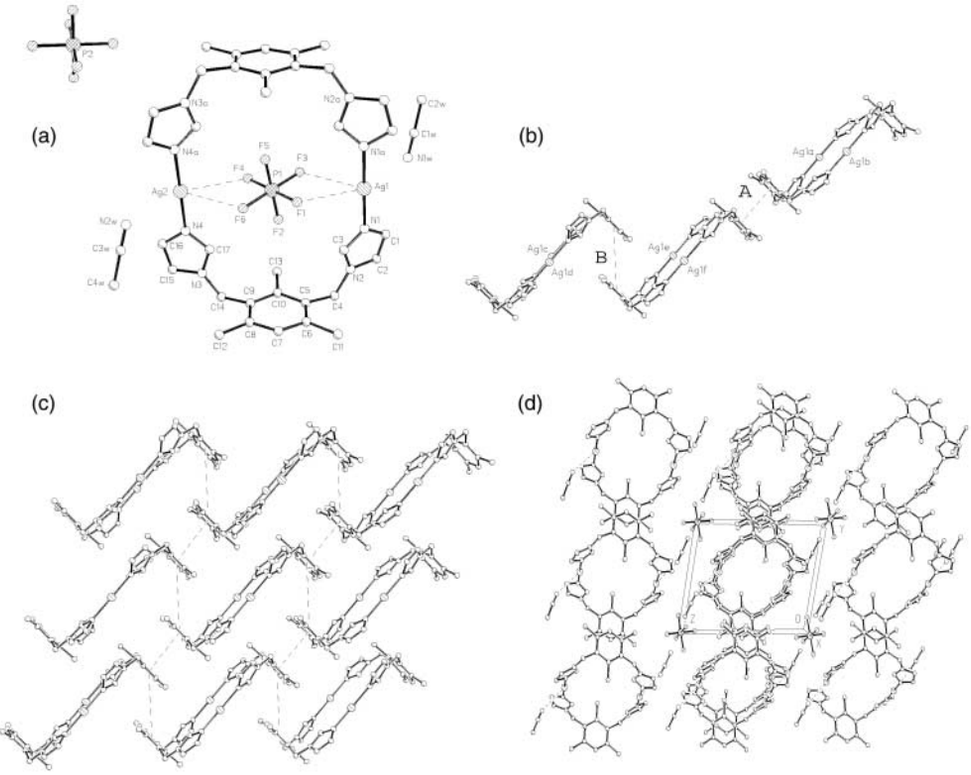

Fig. 1 (a) Perspective view and atomic labelling of the crystal structure of complex **1**. (b) Part of the crystal packing diagram of **1** showing two types of intermolecular $\pi\cdots\pi$ interactions (type A and B). (c) Crystal packing diagram of **1** showing the brick-wall network formed *via* two types of intermolecular $\pi\cdots\pi$ interactions in the *ab* plane. Solvate molecules and anions were omitted for clarity. (d) Packing diagram of the brick-wall layers of **1** in the *yz* plane, encapsulated PF_6^- anions are omitted for clarity.

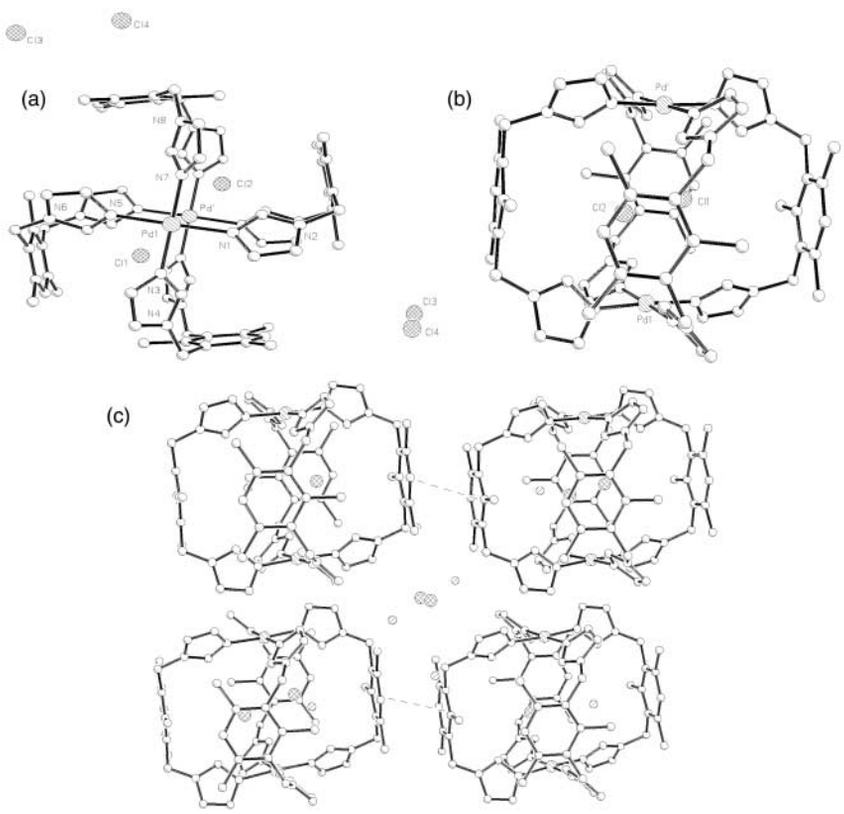

Fig. 2 (a) Crystal structure of **2** (down the Pd–Pd axis). (b) Crystal structure of **2** (in the *ab* plane). The hydrogen atoms and solvate molecules are omitted for clarity. (c) Crystal packing diagram of **2** showing the one-dimensional chain network formed *via* intermolecular $\pi\cdots\pi$ interactions in the *ab* plane.

encapsulated PF_6^- anions and non-coordinated acetonitrile molecules are located.

The structure of complex **2** is shown in Fig. 2. The bitmb ligand is in *cis*,*cis*-conformation (V-form) and each attached to two Pd atoms by the N atoms of the two imidazole arms. The two imidazolyl rings of each bitmb are inclined to the phenyl ring at angles of 83.6 and 103.8°, respectively, with a dihedral angle of 57° between the two terminal imidazolyl rings. The Pd

atom is coordinated by four N atoms from four independent bitmb ligands, while the Cl^- anions and water molecules are uncoordinated. The coordination environment of the palladium(II) atoms is a distorted square-planar N_4 geometry in which the N–Pd–N bond angles vary from 89.09(8) to 178.70(8)° as shown in Table 2. The Pd–N bond lengths range from 2.004(2) to 2.0174(19) Å similar to the reported palladium(II) complexes with the same PdN_4 binding site; for example, the twin-cage complex $[Pd_3(bitmb)_4Cl_4]Cl_2$ exhibits a Pd–N bond length range of 2.014(3)–2.021(3) Å,[12] and a Pd_2L_4 (L = 1,4-bis(3-pyridyloxy)benzene) cage exhibits an Pd–N bond length range of 2.008(6)–2.032(5) Å.[18] Four bitmb and two Pd atoms form an M_2L_4 cage (Fig. 2), in which two disordered Cl^- anions and a water molecule are encapsulated. External to the cage are two further Cl^- anions, seven water molecules and one and a half acetonitrile molecules (water and acetonitrile molecules not shown). Looking down the Pd–Pd axis (Fig. 2(a)), this M_2L_4 cage resembles a paddlewheel, and the two pairs of cofacial benzene rings are in a *trans* conformation with nearest distances of 10.54 and 10.58 Å, respectively. The Pd···Pd separation is 6.93 Å and the dimension of the cage is 6.93 × 10.54 × 10.58 Å, which is slightly larger than for the complex $C_{68}H_{54}F_{24}N_{10}O_8P_4Pd_2$, with a cavity of size 8.840 × 8.849 × 8.925 Å as reported by McMorran and Steel.[18a] The packing arrangement of the M_2L_4 cages is illustrated in Fig. 2(c). Along the *a* axis, the phenyl ring of one cage is parallel to an adjacent phenyl ring of another cage with an inter-plane separation of 3.96 Å, showing π···π interaction between the two rings. Thus, the M_2L_4 cage molecules are linked by π···π interactions, forming an interesting one-dimensional chain along the *a* axis; all the solvent molecules (water and acetonitrile, not shown) and unencapsulated chlorate anions lie in the interspaces of the chains.

Fig. 3 shows the single-crystal structure of complex **3**, in which each Zn is four-coordinated by two nitrogen atoms of two bitmb ligands, an oxygen atom of an acetate anion and an oxygen atom of a disordered solvent ethanol molecule. The coordination geometry of the metal ion is distorted tetrahedral with coordination angles varying from 100.0(3) to 120.9(3)° (Table 2) and the dihedral angle of the two imidazole rings which are coordinated to the same zinc atom is 57°. As shown in Fig. 3(b), each ethanol molecule has two positions with site occupancy factors (s.o.f.s) of 0.5, and is mono-coordinated to zinc atoms with a bond length of 2.223(11) Å, while each ordered acetate anion is also mono-coordinated to zinc with a bond length of 1.968(6) Å, this Zn–O bond length is slightly longer than that (1.84(2) Å) in the M_3L_2 cage complex.[10] Each bitmb ligand shows a "V-form" and is attached to two zinc atoms by its two imidazolyl arms with bond lengths of 2.018(4) Å, similar to the reported zinc(II) complexes with the same ZnN_2O_2 bonding site; for example $[Zn_3(tib)_2(CH_3CO_2)_6]$ exhibits an Zn–N bond length of 2.022(7) Å.[10] Thus, a one-dimensional zigzag polymer chain has been formed along the *b* axis, in which all the phenyl rings of the bitmb are coplanar and with a nearest center-to-center separation of 12.150 Å, which is equal to the nearest intrachain Zn···Zn separation. A C_2H_5O–H···OH hydrogen bond is formed between the OH^- anions and the disordered ethanol molecules, with an O···O distance of 2.122 Å. A further H_2C–H···CH_3 hydrogen bond may be formed between the hydrogen atoms and carbon atoms of disordered ethanol molecules from two adjacent chains with a C···C separation of 1.814 Å, and the novel one-dimensional double polymer chain is shown in Fig. 3(b). The packing arrangement of the zinc-based polymer complex **3** is shown in Fig. 3(c) and is different from that found previously.[23]

Fig. 4 shows the crystal structure of complex **4**, in which each Co is six-coordinated by six N atoms from four different bitmb ligands and two acetonitrile molecules with the N–Co–N bond angles varying from 88.29(13) to 180.00(19)° as shown in Table 2. Therefore the coordination environment of the cobalt atom

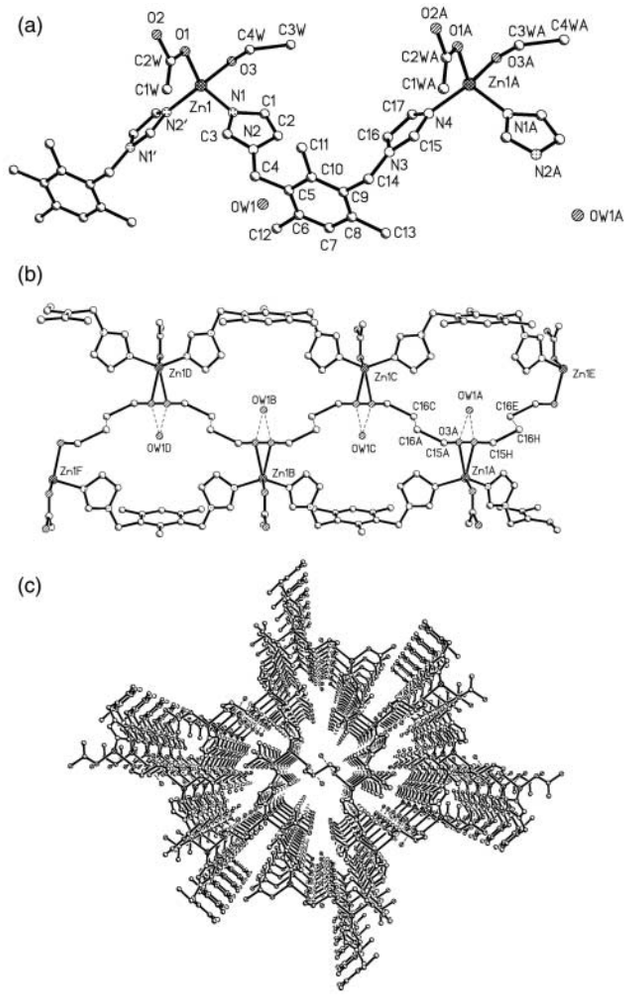

Fig. 3 (a) Crystal structure of **3** with the atom numbering scheme. (b) A novel one-dimensional double polymer chain formed *via* hydrogen bonds along the *b* axis. (c) Crystal packing diagram of **3** in the *xz* plane. Hydrogen bonds are indicated by dashed lines.

can be regarded as distorted octahedral with the Co–N bond distances ranging from 2.117(3) to 2.187(4) Å. The basal plane of the cobalt center is defined by four N atoms from four bitmb ligands; the axial positions are occupied by two N atoms from two acetonitrile molecules. The average Co–N bond distances of the cobalt center in the basal plane is 2.123(3) Å, while the average bond length of the axial positions is 2.187(3) Å. The axial Co–N bond distances are thus approximately 0.06 Å longer than those of the basal plane.[24] Each bitmb ligand has an extended geometry with "Z" shape (*trans*,*trans*-conformation) since the two terminal imidazole groups are in the opposite direction with reference to the phenyl plane and serve to attach two Co atoms. The two imidazolyl rings of each bitmb are inclined to the phenyl ring at angles of 81.6 and 93.1°, respectively, and with a dihedral angle of 107.2° between the two terminal imidazolyl rings. As a result, two bitmb ligands and two Co atoms form an M_2L_2 dimeric macrocycle[15] and two adjacent macrocyles share a cobalt atom and such units form an infinite one-dimensional chain (Fig. 4(a)). It has also been reported that 4,4′-bis(imidazo-1-ylmethyl)biphenyl forms an infinite poly-cage by assembly with $MnCl_2$.[25] In the present case the infinite 1D polymeric chain can be regarded as a poly-macrocycle as illustrated in Fig. 4(a). The distance between Co and Coa is 12.616 Å and the nearest distance between two coplanar phenyl rings defined by the methyl groups C2 and C2a is 3.709 Å. Whilst there are no intramolecular π–π interactions, the packing of the 1D poly-macrocycle chains is partly controlled by such interactions. As shown in Fig. 4(b), the poly-macrocycle chains self-assemble

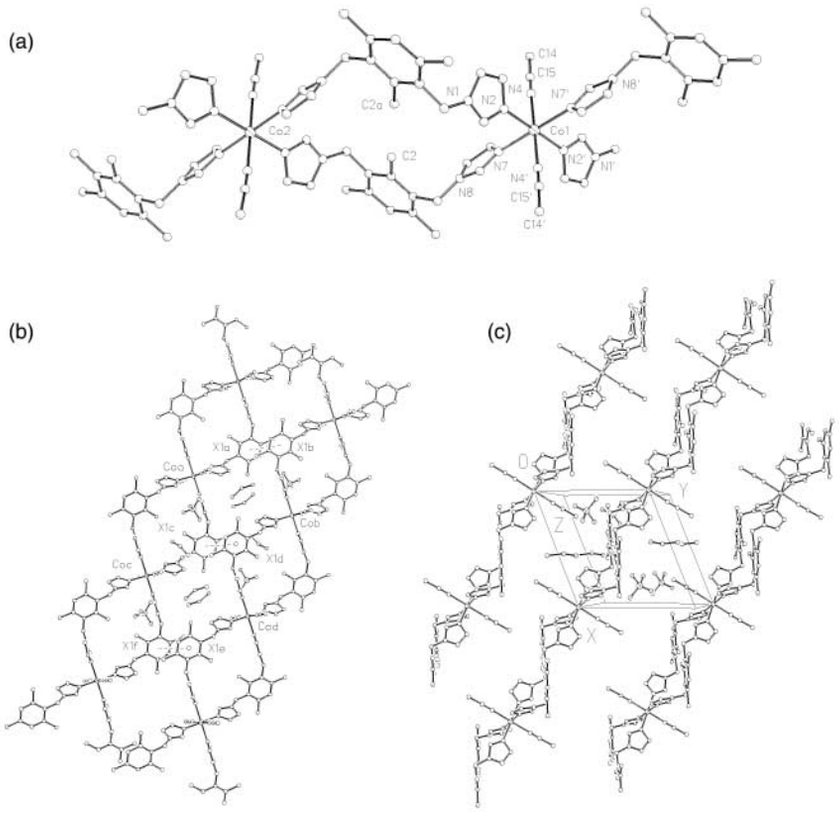

Fig. 4 (a) Cation part of the local co-ordination around the cobalt(II) atoms in **4**. (b) Crystal packing diagram of the two-dimensional grid network formed *via* intermolecular π···π interactions (indicated by dashed lines) in the *ac* plane. (c) Crystal packing diagram of the two-dimensional grid network in the *xy* plane.

into a two-dimensional network within which there is π–π stacking between phenyl rings of adjacent chains (center-to-center distance = 3.511 Å). Quadrangular cavities are formed between adjacent chains and the dimensions are defined by the interchain Co···Co separation (Coa···Cob, 11.82 Å) and the separation of the intermacrocycle phenyl rings (centoid-to-centroid distances, *x*1a–*x*1c = *x*1b–*x*1d = 12.61 Å). The layers repeat in an -··-ABAB-··- stacking sequence along the *b* axis as shown in Fig. 4(c). There is a large interspace between two adjacent layers within which the ethanol molecules and perchloride anions are accommodated.

Discussion

In comparing complexes **1**–**4**, it is interesting that **1** and **2** are finite structures but that **3** and **4** are infinite structures. In complexes **1** and **2**, the coordination geometries of silver and palladium are linear N_2 or square-planar N_4, respectively, while in complexes **3** and **4**, the coordination geometries of zinc and cobalt are tetrahedral N_2O_2 or octahedral N_6, respectively. This result shows that the coordination geometry of the metal atoms play an important role in the construction of supramolecular complexes. The M···M separation between two metal atoms linked with a bitmb in complexes **1**, **2**, **3** and **4** is 7.75, 6.93, 12.150, and 12.616 Å, respectively. This implies that the bitmb ligand in the infinite networks **3** and **4** appear more stretched out than in the finite supramolecular complexes **1** and **2**.

The ditoptic ligand bitmb is versatile and affords two types of conformations, *i.e. cis*,*cis*-conformation (V-form) and *trans, trans*-conformation (Z-form) when coordinated with different transition metal complexes. The bitmb ligand shows *cis*,*cis*-conformation when coordinated with silver(I), palladium(II) or zinc(II) ions where the coordination number of metal ions is 2, 4 and 4, respectively, but for cobalt(II) ion, the bitmb exhibits a *trans, trans*-conformation where the coordination number of cobalt(II) is 6. Our previous work [11] also shows that the bitmb ligand is in the *cis*,*cis*-conformation when coordinated with palladium(II) where the coordination number of the metal ion is 4. The results indicate that the conformations of the bitmb ligand are obviously controlled by the coordination number of the central metal ions. Further studies of the reaction of the bitmb ligand with other transition metal ions are in progress.

Properties

The solid state IR spectra (KBr disk) of complexes **1**–**4** were measured. Complex **1** showed a very strong band at 838 cm^{-1} and a strong band at 558 cm^{-1} for PF_6^-. Complex **3** shows carboxyl antisymmetric (ν_{asym}) and symmetric (ν_{sym}) vibrations at 1619, 1590 cm^{-1} and 1394 cm^{-1} for mono-coordinated acetate anions in the infrared (IR) spectrum, respectively. The separation between the ν_{asym} and ν_{sym} frequencies is similar to that found in our previous work,[8] indicating direct coordinative bonding between the acetate anions and the Zn(II) ions, which is in agreement with the crystallographic results. There was a sharp $\nu_{C\equiv N}$ at 2029 cm^{-1} in complex **4** which is consistant with the structural results and a very sharp band at 1091 cm^{-1} and a strong band at 623 cm^{-1} for ClO_4^-.

Conclusion

Four novel supramolecular complexes of the bitmb ligand with silver(I), palladium(II), zinc(II) and cobalt(II) salts have been prepared and characterized by single crystal X-ray diffraction. In the solid state, the topology is found to be dependent on the coordintion geometry of the metal atoms. With bitmb, an M_2L_2 cyclic dimer and an M_2L_4 cage form with Ag(I) (linear N_2 geometry) or Pd(II) (square-planar N_4 geometry), while an 1D zigzag chain network and an infinite 1D poly-macrocycle chain network form with Zn(II) (tetrahedral N_2O_2 geometry) or Co(II) (octahedral N_6 geometry). It is also found that the conformations of the bitmb ligand are obviously controlled by the coordination number of the central metal ions. When coordinated to silver (coordination number $n = 2$), palladium ($n = 4$) or

zinc ($n = 4$), bitmb has a *cis*,*cis*-conformation, but in the case of cobalt ($n = 6$), bitmb adopts a *trans*,*trans*-conformation. Therefore, the results of this study not only illustrate that the metal ions play important roles in the construction of supramolecular complexes, but also the $\pi\cdots\pi$ interactions together with the hydrogen bonds co-affect inorganic supramolecular formation.

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