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One-pot conversion of tetraiminodiphenols to diiminodiaminodiphenols *via* methyl transfer at aluminium

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The [2 + 2] macrocyclic Schiff base $\{[2\text{-}(OH)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1,3\text{-}CH][(CH_2CH_2)(2\text{-}C_6H_4N)_2]\}_2$ (**1**) is readily converted to the diiminodiamine $\{[2\text{-}(OH)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1\text{-}(CH)\text{-}3\text{-}C(Me)H][(CH_2CH_2)(2\text{-}(N)\text{-}2'\text{-}C_6H_4NH)_2]\}_2$ (**2**) *via* methyl group transfer from Me_3Al (four equivalents) and subsequent hydrolysis. When compound **1** is reacted with two equivalents of Me_3Al, the dinuclear complex $\{(Me_2Al)[2\text{-}(O)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1,3\text{-}(CH)_2][(CH_2CH_2)(2\text{-}C_6H_4)_2N)_2]\}_2$ (**3**) is formed. The structures of the macrocycles **1** and **2** are described (in the case of **1**, the toluene solvate has also been structurally characterised).

Keywords: Schiff base; macrocycle; trimethylaluminium; imine; amine

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Introduction

Over the years, Schiff-base-type compounds have primarily attracted attention due to their biological activity (*1–5*). Macrocyclic Schiff bases have the added advantage of possessing multiple binding sites, the positions of which can be varied by judicious choice of precursor (*6–8*). Our interest in such systems stems from their potential to coordinate simultaneously multiple, catalytically active metal centres, and the potential ability to tune the resulting cooperative effects. With this in mind, we have embarked upon a program to investigate structure–activity relationships during ε-caprolactone polymerisation using macrocyclic Schiff base procatalysts bearing multiple main group centres (*9*). Our starting point is the simplest of this macrocyclic family, the so-called Robson-type macrocycles (*10–12*), resulting from the [2 + 2] condensation of a diamine with a dialdehyde (in this particular case, a 1,3-diformylphenol). Template syntheses have commonly been employed for such ligand systems (*13–17*); however, occasionally it has been possible to form the macrocycle in high yield in the absence of metal (and even acid catalyst) (*18*, *19*). Herein, we show that use of the ethylene-bridged dianiline $[(CH_2CH_2)(2\text{-}C_6H_4NH_2)_2]$ and the dialdehyde $[2\text{-}(OH)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1,3\text{-}(CHO)_2]$ in refluxing toluene readily affords the [2 + 2] macrocyclic Schiff base **1**, $\{[2\text{-}(OH)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1,3\text{-}CH][(CH_2CH_2)(2\text{-}C_6H_4N)_2]\}_2$, in a template-free fashion. Furthermore, subsequent treatment with four equivalents of trimethylaluminium affords regiospecific methyl transfer yielding on hydrolysis the diiminodiamine macrocycle **2**, $\{[2\text{-}(OH)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1\text{-}(CH)\text{-}3\text{-}C(Me)H][(CH_2CH_2)(2\text{-}(N)\text{-}2'\text{-}C_6H_4NH)_2]\}_2$, in *ca* 74% yield. Reaction of compound **1** with two equivalents of trimethylaluminium yields, after workup, the tetraimino supported dinuclear complex **3**, $\{(Me_2Al)[2\text{-}(O)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1,3\text{-}(CH)_2][(CH_2CH_2)(2\text{-}C_6H_4)_2N)_2]\}_2$, in good yield (*ca* 62%).

Experimental section

General

No special precautions were used when preparing ligand **1**. All manipulations involving Me_3Al were carried out under an atmosphere of dinitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. NMR spectra were recorded at room temperature on a Varian VXR-400S spectrometer at 400 MHz (^{1}H) or a Gemini 300 NMR spectrometer at 300 MHz (^{1}H). The ^{1}H NMR spectra were calibrated against the residual protio impurity of the deuterated solvent. Elemental analyses were performed by the elemental analysis service of the London Metropolitan University. IR spectra (powder) were recorded on a PerkinElmer Spectrum BX FT-IR System equipped with an ATR probe.

Materials

2-Hydroxy-5-*tert*-butyl-1,3-benzenedicarboxaldehyde (*20*) and $[(CH_2CH_2)(2\text{-}C_6H_4NH_2)_2]$ (*21*) were prepared according to the reported procedures. All other chemicals were obtained commercially and used as received, unless stated otherwise.

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Synthesis of Schiff base macrocycles and complex **3**

Compound **1**

2-Hydroxy-5-*tert*-butyl-1,3-benzenedicarboxaldehyde (0.81 g, 3.9 mmol) and [$(CH_2CH_2)(2\text{-}C_6H_4NH_2)_2$] (0.88 g, 4.2 mmol) were refluxed in toluene for 24 h. The mixture was allowed to cool to room temperature and yellow crystals of **1** slowly formed. The solid was filtered and dried *in vacuo* overnight. Recrystallisation from acetonitrile or toluene afforded **1** as pale yellow prisms (yield 1.23 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (br s, 4H, N=C*H*), 7.47–6.47 (m, 20H, Ar-*H*), 3.30 (br s, 8H, CH_2), 1.43 (s, 18H, $C(CH_3)_3$) ppm; elemental analysis calculated for $C_{52}H_{52}N_4O_2$: C 81.64, H 6.85, N 7.32; found C 81.79, H 6.76, N 7.16%; MS (ES +) *m/z*: 765.4 $[M + H]^+$; IR (ATR): 2961(w), 1629(s), 1588(m), 1573(m), 1471(m), 1447(s), 1395(w), 1352(w), 1312(w), 1288(w), 1262(w), 1202(m), 1176(m), 1122(w), 1089(w), 1036(m), 1008(m), 973(w), 915(w), 858(w, 798(m), 722(m), 738(s), 694(w), 647(w), 633(w), 612(w) cm^{-1}; m.p. 344°C (dec.).

Compound **2**

Compound **1** (1.00 g, 1.3 mmol) was dissolved in dry toluene (30 mL). Me_3Al (2 M in hexanes; 2.9 mL, 5.8 mmol) was added while stirring. The orange solution was stirred at room temperature for 30 min and then refluxed for 12 h. After the removal of solvent, the resulting solid was washed with hot acetonitrile (dry; 3 × 30 mL) and dissolved in dry dichloromethane (20 mL). Degassed water (5 mL) was added dropwise while stirring. The solution was stirred for 1 h. The organic phase was isolated and the aqueous phase extracted with an additional 20 mL of dichloromethane. The organic layers were combined and dried over magnesium sulfate. Removal of solvent yielded a yellow solid. Recrystallisation from acetonitrile afforded **2** as pale yellow prisms (0.77 g, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.56 (s, 2H, C*H*=N), 7.43 (s, 2H, C_6H_2), 7.27 (s, 2H, C_6H_2), 7.16 (pt, $J_{obs} = 7.7$ Hz, 2H, CH=N*p*-C_6H_4), 7.01 (m, 4H, CH=N*o*,*m*-C_6H_4), 6.93 (d, $J = 7.5$ Hz, 2H, HN*m*-C_6H_4), 6.87 (pt, $J_{obs} = 7.5$ Hz, 2H, HN*m*-C_6H_4), 6.69 (d, $J = 8.1$ Hz, 2H, CH=N*m*-C_6H_4), 6.52 (pt, $J_{obs} = 7.4$ Hz, 2H, HN*p*-C_6H_4), 6.26 (d, $J = 7.4$ Hz, 2H, HN*o*-C_6H_4), 5.42 (d, $J = 10.3$ Hz, 2H, N*H*), 4.73 (m, 2H, C*H*-CH_3), 3.20 (d, $J = 9.8$ Hz, 2H, CH_2), 3.09–2.88 (m, 4H, CH_2), 2.50 (d, $J = 9.8$ Hz, 2H, CH_2), 1.74 (d, $J = 6.7$ Hz, 6H, CH-CH_3), 1.37 (s, 18 H, $C(CH_3)_3$) ppm; MS (ES +) *m/z*: 797.6 $[M + H]^+$; IR (ATR): 3300(w, broad), 2960(w), 2358(w), 1627(m), 1588(w), 1570(w), 1484(w), 1450(m), 1354(w), 1262(m), 1205(m), 1088(w, 1034(w), 1010(m), 970(w), 860(m), 800(m), 770(m), 725(s), 635(w), 613(w) cm^{-1}; m.p. 166°C.

Compound **3**

Compound **1** (1.00 g, 1.3 mmol) was dissolved in dry toluene (30 mL). Me_3Al (2 M in hexane; 1.4 mL, 2.8 mmol) was added while stirring. The mixture was stirred at room temperature for 10 min and then refluxed for 12 h. After the removal of solvent, the crude material was washed with hot acetonitrile (30 mL) affording **3** as a yellow powder (yield 0.70 g, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, $J = 2.5$ Hz, 2H, C_6H_2), 8.14 (s, 2H, C*H*=N), 7.58 (d, $J = 7.7$ Hz, 2H, AlN-*o*-C_6H_4), 7.41 (pseudo t, $J = 7.7$ Hz, 2H, AlN-*m*-C_6H_4), 7.24 (m, 2H, AlN-*p*-C_6H_4), 7.18 (pseudo t, $J = 7.5$ Hz, 2H, *N*-*m*-C_6H_4), 7.02 (d, $J = 7.5$ Hz, 2H, *N*-*o*-C_6H_4), 6.91 (d, $J = 2.5$ Hz, 2H, C_6H_2), 6.88 (pseudo t, $J = 7.5$ Hz, 2H, *N*-*p*-C_6H_4), 6.76 (d, $J = 7.8$ Hz, 2H, AlN-*m*-C_6H_4), 6.50 (d, $J = 7.5$ Hz, 2H, *N*-*m*-C_6H_4), 6.29 (s, 2H, C*H*=N), 3.90 (td, $J_t = 3.7$ Hz, $J_d = 12.1$ Hz, 2H, CH_2), 3.55 (dt, $J_d = 4.0$ Hz, $J_t = 12.5$ Hz, 2H, CH_2), 3.04 (td, $J_t = 3.7$ Hz, $J_d = 13.7$ Hz, 2H, CH_2), 2.62 (dt, $J_d = 3.7$ Hz, $J_t = 12.5$ Hz, 2H, CH_2), 1.49 (s, 18H, $C(CH_3)_3$), −0.77 (s, 6H, $AlCH_3$), −1.15 ppm (s, 6H, $AlCH_3$); elemental analysis calculated for $C_{56}H_{62}Al_2N_4O_2$: C 76.69, H 7.13, N 6.39; found: C 76.60, H 6.99, N 6.28%; MS (EI) *m/z*: 877.4 $[M + H]^+$; IR (nujol mull, KBr): 1624(m), 1606(w), 1594(m), 1561(w), 1546(m), 1295(w), 1261(m), 1178(m), 1086(m), 1037(w), 1017(w), 992(w), 841(m), 809(m), 765(m), 750(w), 702(w), 682(m) cm^{-1}; m.p. >350°C.

Crystal structure analyses

Crystals were mounted in oil on glass fibres and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3 CCD diffractometer, or for **1**.2(C_7H_8) on a Bruker–Nonius Roper CCD diffractometer, equipped with Mo-Kα radiation [λ(MoKα) = 0.71073 Å] and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans.

Data for **1** and **2**.3(CH_3CN) were processed using the CrysAlis-CCD and CrysAlis-RED (*22*) programs, or for **1**.2(C_7H_8) in DENZO/SCALEPACK (*23*). The structures were determined by the direct methods routines in the SHELXS program (*24*) and refined by full-matrix least-squares methods, on F^2's, in SHELXL (*24*). The non-hydrogen atoms were refined with anisotropic thermal parameters. The phenol and amino hydrogen atoms were located in difference maps and were refined freely; all remaining hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms. CCDC-693022–693024 contain the supplementary data for **2**.3(CH_3CN), **1**, and **1**.2(C_7H_8), respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

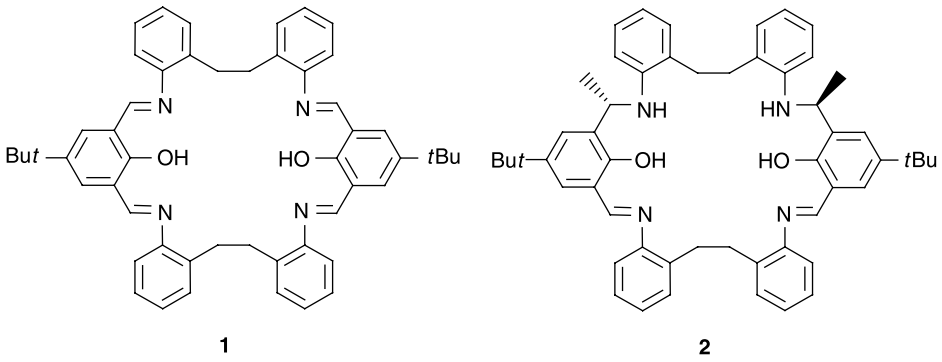

Chart 1. Schiff base macrocycles **1** and **2**.

Results and discussion

Synthesis and crystal structures

The Schiff base macrocycle **1** (Chart 1) is readily available in high yield (*ca* 82%) on refluxing (in toluene, for 24 h) the dianiline $[(CH_2CH_2)(2\text{-}C_6H_4NH_2)_2]$ and 2-hydroxy-5-*tert*-butyl-1,3-benzenedicarboxaldehyde $[2\text{-}(OH)\text{-}5\text{-}(t\text{Bu})C_6H_2\text{-}1,3\text{-}(CHO)_2]$. The [2 + 2] condensation product **1** can be recrystallised from toluene as its toluene solvate (Figure 1) or from acetonitrile as the solvent-free macrocycle (Figure 2). Selected bond lengths and angles for both forms of **1** are presented in Table 1, with crystallographic parameters collated in Table 2.

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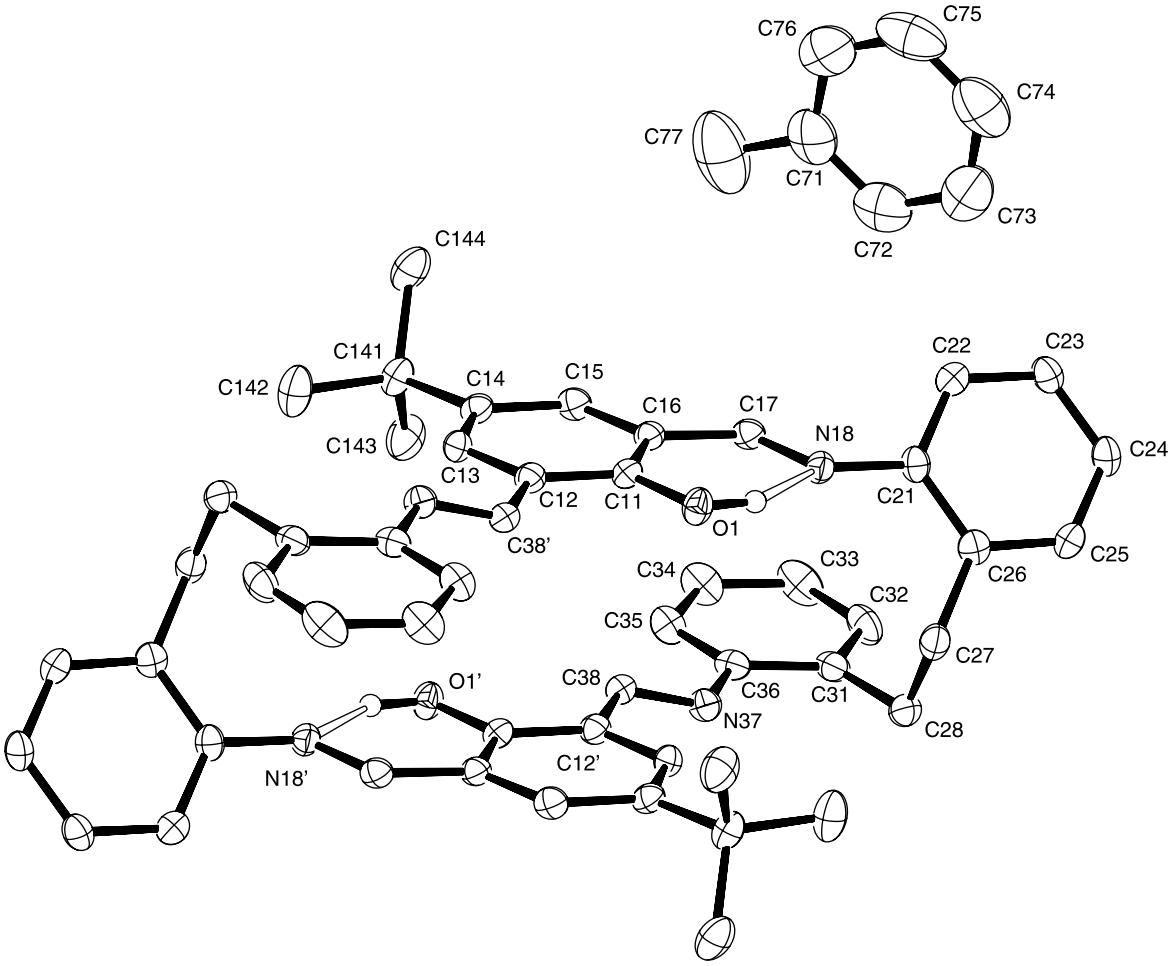

Figure 1. X-ray crystal structure of **1**.2(C_7H_8) with the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms (other than those involved in hydrogen bonds) have been omitted for clarity.

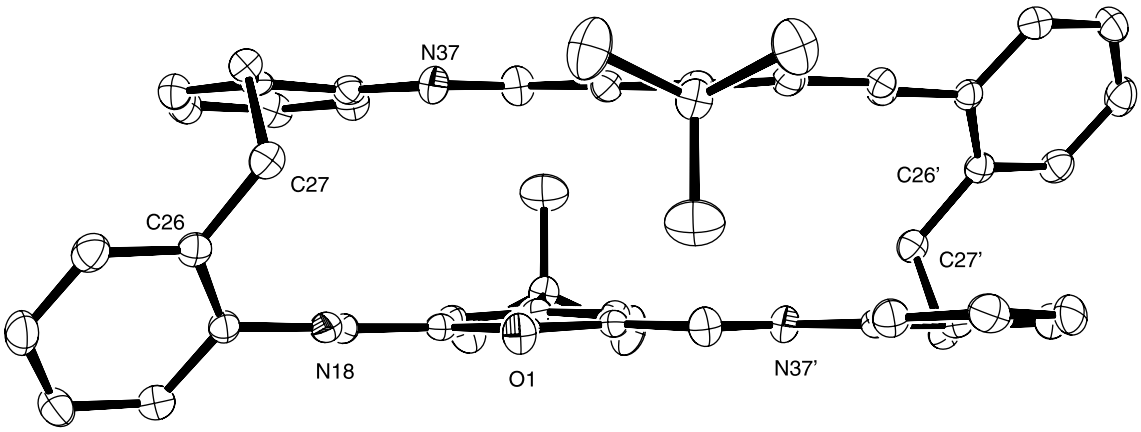

Figure 2. X-ray crystal structure of **1** (this structure is essentially identical to that shown in Figure 1, an alternative view is shown here). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

In both solvate and solvent-free structures, the molecule of **1** lies about a centre of symmetry. The dihedral angle C(36)—N(37)—C(38)—C(12′) is close to 180° (−177.84(18) and −177.60(13) for **1**.2(C_7H_8) and **1**, respectively) and the rings of C(11′–16′) and C(31–36) are close to coplanar, and overlap the corresponding plane on the opposite side of the molecule. There is limited overlap of the individual rings, but C(38′) is 3.15 Å above the C(11′–16′) plane, and C(17′) is 3.32 Å below the plane of C(31′–36′). The remaining rings, of C(21–26) and its symmetry related ring, link the two major planes. The toluene solvent molecules have no close interaction with the macrocyclic ring. Unsurprisingly, the bond lengths and angles are very similar for the structures of **1** and **1**.2(C_7H_8). These compounds display a strong intramolecular hydrogen bond (and its symmetrically equivalent) involving the phenolic hydrogen and an imino nitrogen (H(1)···N(18) 1.74(3) and 1.71(2) Å, O(1)—H(1)···N(18) 152(3) and 149.9(17)° for **1**.2(C_7H_8) and **1**, respectively).

Table 1. Selected bond lengths and angles for **1**.2(C_7H_8), **1** and **2**.3(CH_3CN; Å, °).

	1.2(C_7H_8)	**1**	**2**.3(CH_3CN)
C(17)—N(18)	1.283(3)	1.2795(18)	1.2815(19)
N(18)—C(21)	1.417(3)	1.4206(17)	1.422(2)
N(37)—C(38)	1.277(3)	1.2554(17)	1.2863(19)
C(36)—N(37)	1.414(3)	1.4182(17)	1.4178(19)
C(16)—C(17)	1.454(3)	1.4514(18)	1.457(2)
C(12)—C(38′)	1.470(3)	1.4668(19)	
C(47)—N(48)			1.454(2)
N(48)—C(51)			1.379(2)
C(66)—N(67)			1.395(2)
N(67)—C(68)			1.4656(19)
C(38)—C(42)			1.456(2)
C(46)—C(47)			1.525(2)
C(12)—C(68)			1.518(2)
H(1)···N(18)	1.74(3)	1.71(2)	1.60(2)
H(4)···N(37)			1.75(2)
H(67)···O(1)			2.37(2)
H(48)···O(4)			2.58(2)
C(17)—N(18)—C(21)	120.12(17)	121.20(13)	120.41(14)
C(38)—N(37)—C(36)	121.46(18)	121.64(13)	120.41(14)
C(31)—C(28)—C(27)	114.13(18)	115.27(12)	112.60(13)
O(1)—H(1)···N(18)	152(3)	149.9(17)	155(2)
O(4)—H(4)···N(37)			146(2)
N(67)—H(67)···O(1)			111.5(12)
N(48)—H(48)···O(4)			107.5(15)
C(36)—N(37)—C(38)—C(12′)	−177.84(18)	−177.60(13)	

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Table 2. Crystal and structure refinement data for **1**, **1**.2(C_7H_8) and **2**.3(CH_3CN).

Compound	**1**	**1**.2(C_7H_8)	**2**.3(CH_3CN)
Formula	$C_{52}H_{52}N_4O_2$	$C_{52}H_{52}N_4O_2$, 2(C_7H_8)	$C_{54}H_{60}N_4O_2$, 3(C_2H_3N)
Formula weight	765.0	949.2	920.2
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Unit cell dimensions			
a (Å)	7.2342(3)	7.8251(2)	14.0953(4)
b (Å)	9.9406(4)	20.5549(7)	14.3270(6)
c (Å)	14.3243(5)	17.1484(6)	14.9271(6)
α (°)	96.779(3)	90	64.240(4)
β (°)	91.693(3)	101.485(2)	82.897(3)
γ (°)	91.324(4)	90	82.141(3)
V (Å^3)	1022.08(7)	2702.99(15)	2682.39(17)
Z	1	2	2
Temperature (K)	140(1)	120(2)	140(1)
Calculated density (g cm^{-3})	1.243	1.166	1.139
Absorption coefficient (mm^{-1})	0.076	0.070	0.070
Transmission factors (max./min.)	1.048 and 0.959	1.00 and 0.694	1.045 and 0.962
Crystal size (mm)	0.41 × 0.31 × 0.12	0.36 × 0.1 × 0.08	0.4 × 0.20 × 0.13
θ (max) (°)	27.5	25.0	27.5
Reflections measured	15,129	16,292	34,729
Unique reflexions	4640	4728	12,202
R_{int}	0.051	0.060	0.060
Reflections with $F^2 > 2\sigma(F^2)$	2810	3723	6773
Number of parameters	266	330	641
R_1 [$F^2 > 2\sigma(F^2)$]	0.043	0.059	0.047
R_1 (all data)	0.089	0.082	0.109
wR_2 (all data)	0.098	0.130	0.102
GOOF, S	0.905	1.061	0.881
Largest difference peak and hole (e Å^{-3})	0.21 and −0.18	0.21 and −0.25	0.28 and −0.23

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Reaction of **1** with four equivalents of trimethylaluminium in refluxing toluene followed by hydrolysis readily afforded the imino/amino macrocycle **2** in high yield (*ca* 74%). The formation of **2** involves an intramolecular regioselective methyl transfer at aluminium to two imine moieties of the macrocycle to afford an intermediate dinuclear complex {(Me_2Al)[2-(*O*)-5-(*t*Bu)C_6H_2-1-(CH)-3-C(Me)H][(CH_2CH_2)(2-(*N*)-2′-$C_6H_4NH)_2$]}$_2$ (*25*). Such methyl transfers are now well established in α-diimine chemistry (*26*), and more recently for salicylaldimines (*27*), pyridylimines (*28*), pyridylbis(imines) (*29*, *30*) and bis(imino)phenols (*31*). Crystals of **2** suitable for X-ray diffraction study were grown from a saturated acetonitrile solution at room temperature (Figure 3). Selected bond lengths and angles for **2** are given in Table 1, with crystallographic parameters collated in Table 2. Interestingly, reaction of compound **1** with only two equivalents of trimethylaluminium did not give rise to methyl transfer to the imine moieties, but rather afforded the dinuclear complex {(Me_2Al)[2-(*O*)-5-(*t*Bu)C_6H_2-1,3-$(CH)_2$][(CH_2CH_2)(2-$C_6H_4)_2N)_2$]}$_2$ (**3**), as described in Figure 4. The structure of compound **3** was deducted from ^{1}H NMR spectroscopy, mass spectrometry and preliminary X-ray diffraction studies (*32*).

The regiospecific methylation on two imine moieties originally from the same dianiline precursor gives potential C_2 symmetry to compound **2**. The macrocycle **2** exhibits four intramolecular hydrogen bonds; there are two strong hydrogen bonds between the phenolic hydrogens and the neighbouring imino nitrogen atoms (H(4)···N(37) 1.75(2) Å, O(4)—H(4)···N(37) 146(2)° and H(1)···N(18) 1.60(2) Å, O(1)—H(1)···N(18) 155(2)°) and two weak hydrogen bonds between the amino hydrogens and the phenolic oxygens (H(48)···O(4) 2.58(2) Å, N(48)—H(48)···O(4) 107(2)° and H(67)···O(1) 2.37(2) Å, N(67)—H(67)···O(1) 111.5(12)°).

The regiospecificity of the methylation of the imine groups to afford **2** is intriguing. The product resulting (in good yield) from the use of only two equivalents of Me_3Al, namely {(Me_2Al)[2-(*O*)-5-(*t*Bu)C_6H_2-1,3-$(CH)_2$][(CH_2CH_2)(2-$C_6H_4)_2N)_2$]}$_2$, reveals a clear preference for the aluminium centres to bind to the imine groups of the macrocyclic framework derived from the same aniline. Furthermore, the methylation is not dictated by steric factors, and indeed the use of triethylaluminium, Et_3Al, under similar conditions affords the analogous ethylated macrocycle (*9*). We propose that this arrangement with the aluminium centres *ca* 5.78 Å apart allows for

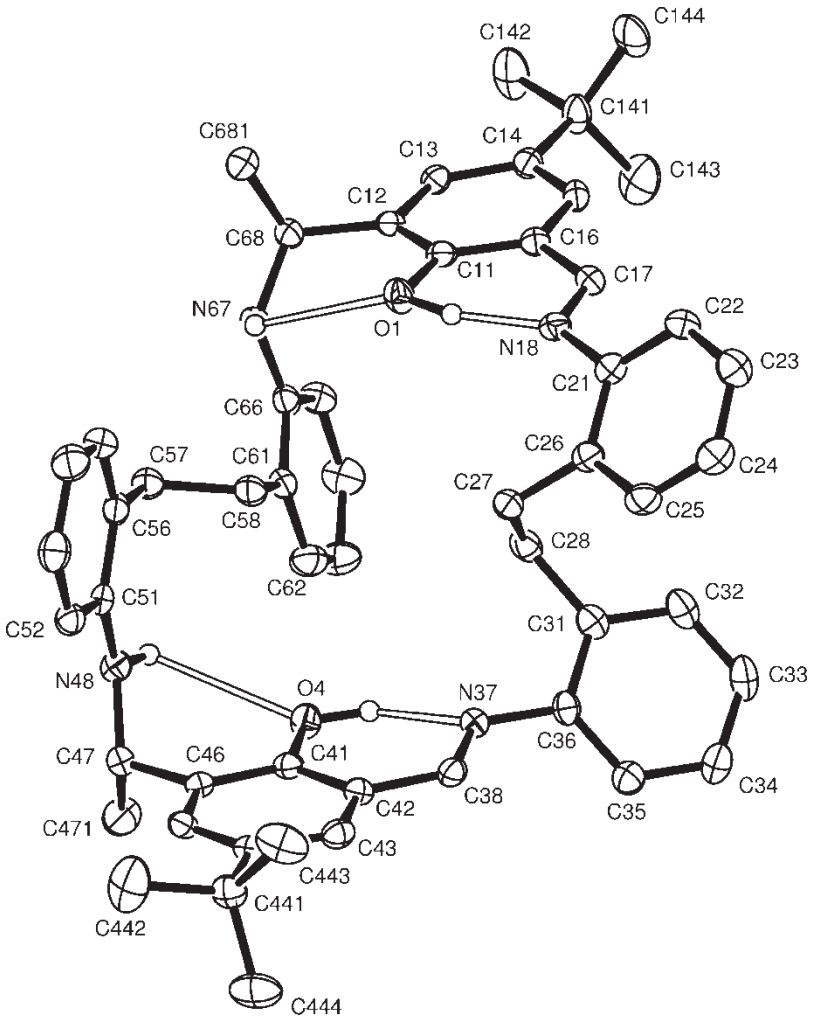

Figure 3. X-ray crystal structure of **2** in **2**.3(CH_3CN) showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms (other than those involved in hydrogen bonds) and acetonitrile molecules have been omitted for clarity.

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a favourable interaction with the two additional equivalents of Me_3Al that are required to bring about the methyl transfer to the imine backbone. Interestingly, our preliminary screening of the ring-opening polymerisation of ε-caprolactone using such organoaluminium-containing macrocycles has suggested there is a cooperative effect in operation when the aluminium centres are predisposed as in **3**.

Spectroscopic and structural studies

The neutral macrocyclic Schiff bases **I**–**XV** presented in Chart 2 were used as comparison points in order to describe the structural and spectroscopic properties of compounds **1**, **1**.2(C_7H_8) and **2**.3(CH_3CN). They all contain the same generic motif 1,3-$(CHN)_2$-C_5H_3X (X = CH, C(OH), N; Figure 5).

For the bis(imino)phenol derivatives **1**, **1**.2(C_7H_8), **2**.3(CH_3CN) and **I**–**IV**, the C═N bond lengths are, in general, noticeably longer (from 1.2554(17) to 1.299(7) Å) (*18,44–47*) than those of the bis(imino)pyridine (compounds **V**–**VII**, **XI**–**XIII** and **XV**, from 1.246(3) to 1.289 Å) (*33–35*, *39–43*) and the bis(imino)benzyl

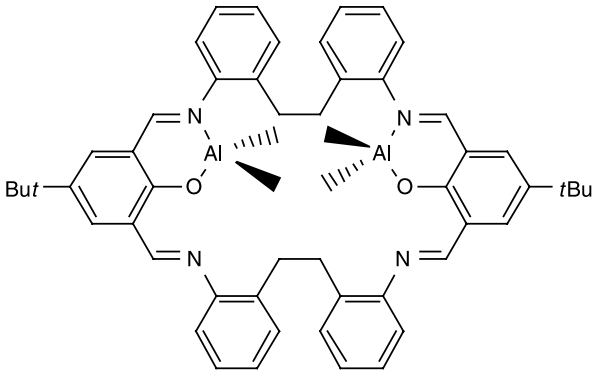
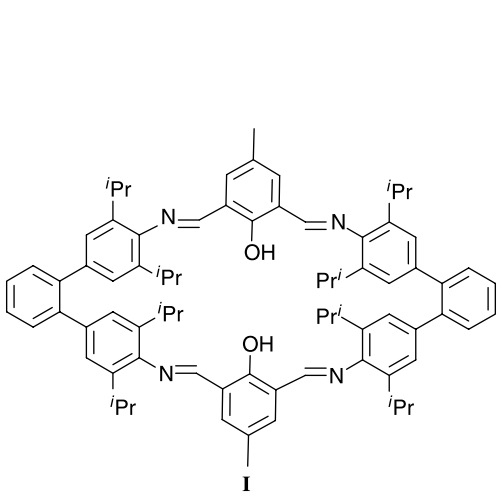
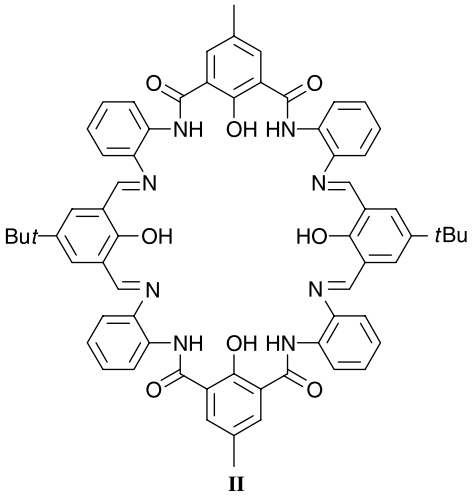


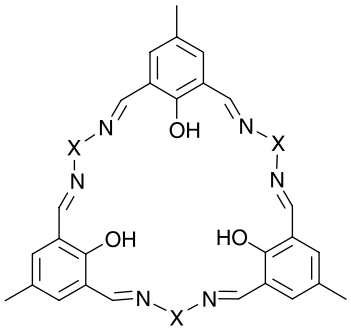
Figure 4. Compound **3**.



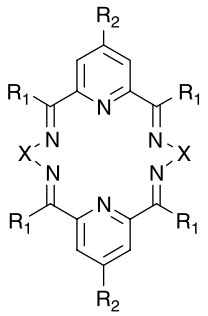
I



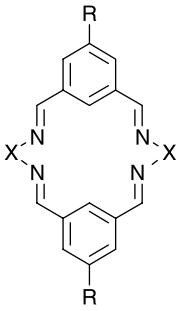
II



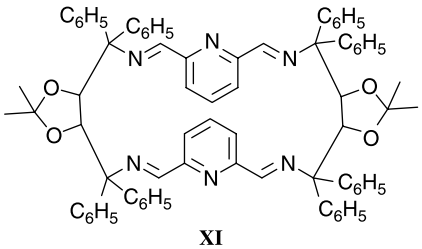
X = 1,2-C_6H_{10} **III**
X = $CH(C_6H_4)CH(C_6H_4)$ **IV**



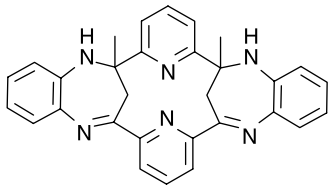
$R_1 = R_2 = H$, X = 1,2-C_6H_4 **V**
$R_1 = R_2 = H$, X = 1,2-C_6H_{10} **VI**
$R_1 = CH_3$, $R_2 = H$, X = 1,2-C_6H_{10} **VII**



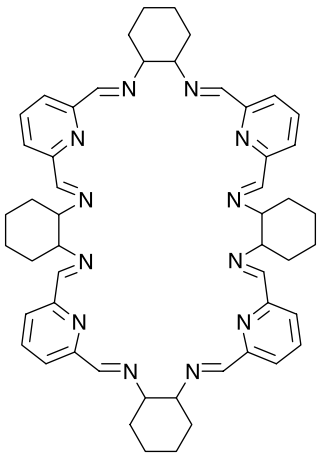
R = H, X = 1,3-$(CH_2)_2$-C_6H_4 **VIII**
R = H, X = $(CH_2)_2NH(CH_2)_2$ **IX**
R = *t*Bu, X = 1,3-$(CH_2)_2$-C_6H_4 **X**



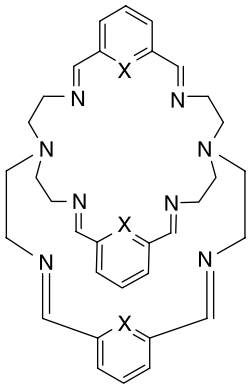
XI



XII



XIII



X = CH **XIV**
X = N **XV**

Chart 2. Macrocyclic Schiff bases used for spectroscopic and structural comparison (*18*, *33–47*).

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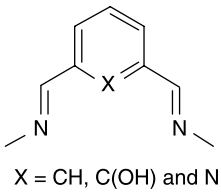

Figure 5. Common motif of the macrocyclic Schiff base selected from the literature.

(compounds **VIII**–**X** and **XIV**, from 1.254(7) to 1.274 Å) (*36*–*38*, *40*, *43*) derivatives. This is owing to the intramolecular hydrogen bonds occurring systematically in bis(imino)phenol-based macrocyclic Schiff bases. The imino C═N bond lengths in both structures of **1** and in **2** are within the range of those reported for bis(imino)phenol-based macrocyclic Schiff bases (*18*, *44*–*47*).

The imino hydrogen chemical shifts (^{1}H NMR) for **1** (8.34 ppm) and **2** (8.56 ppm) are comparable to those of the reported chemical shifts for bis(imino)phenol-based macrocycles (8.12–8.66 ppm) (*18*, *44*–*47*). The imino hydrogen chemical shift in compound **V** is noticeably shifted downfield when compared with compounds **1** and **2** (9.52 for **V** (*35*) and 8.34, 8.56 ppm for **1** and **2**, respectively), owing to conjugation in the former structure.

The $\nu_{C=N}$ for **1** (1629 cm^{-1}) and **2** (1627 cm^{-1}) lie within the range of the reported data for other macrocyclic Schiff bases (*18*, *33*–*47*). Although ν_{N-H} vibrations for compounds **II** (3282 cm^{-1}) (*45*) and **XII** (3336 cm^{-1}) (*33*, *34*) are reported as discrete bands, **2** exhibits a large band at 3300 cm^{-1}.

The cavity sizes measured for **1**, **1**.2(C_7H_8) and **2** (10.7 × 3.6 for **1** and **1**.2(C_7H_8) and 6.5 × 4.3 Å for **2**.3(CH_3CN)) are somewhat smaller than that of compound **I** (16.0 × 5.8 Å), another tetracompartmental ligand based on a bis(imino)phenol moiety, which can accommodate two nickel metals in its cavity (*46*).

Conclusion

The template-free reaction of the dianiline [(CH_2CH_2)(2-$C_6H_4NH_2$)$_2$] and 2-hydroxy-5-*tert*-butyl-1,3-benzenedicarboxaldehyde [2-(OH)-5-(*t*Bu)C_6H_2-1,3-(CHO)] afforded the [2 + 2] macrocyclic Schiff base ligand **1** in excellent yield. Treatment of **1** with four equivalents of Me_3Al and subsequent hydrolysis afforded the imino/amino compound **2**, in good yield, through a regioselective methyl transfer at aluminium. Similar treatment of **1** with two equivalents of Me_3Al afforded the dinuclear complex **3** in good yield. Compounds **1** and **2** are tetracompartmental Robson-type ligands. The ability of **1** and **2** to form complexes, such as compound **3**, with main group metals and the activity of such complexes towards ε-caprolactone ring-opening polymerisation will be reported shortly.

Acknowledgements

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