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

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<td>Redshaw, Carl; University of East Anglia, Chemical Sciences and Pharmacy Arbaoui, Abdessamad; University of East Anglia, Chemical Sciences and Pharmacy Hughes, David; University of East Anglia, Chemical Sciences and Pharmacy</td>
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<tr>
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Graphical abstract
One-pot conversion of tetraiminodiphenols to diiminodiaminodiphenols via methyl transfer at aluminum

Abdessamad Arbaoui, Carl Redshaw* and David L. Hughes

School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, NR4 7TJ, U.K.

Abstract: The [2+2] macrocyclic Schiff base \{2-(OH)-5-(tBu)C₆H₂-1,3-CH][(CH₂CH₂)(2-C₆H₄N)₂]₂ (1) is readily converted to the diimino-diamine \{2-(OH)-5-(tBu)C₆H₂-1-(CH)-3-C(Me)H][(CH₂CH₂)(2-(N)-2′-C₆H₄NH)₂]₂ (2) via methyl group transfer from Me₃Al (four equivalents) and subsequent hydrolysis. When compound 1 is reacted with two equivalents of Me₃Al, the dinuclear complex \{Me₂Al[2-(O)-5-(tBu)C₆H₂-1,3-(CH)₂][(CH₂CH₂)(2-C₆H₄N)₂]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 characterized).

Keywords: Schiff base; Macrocycle; Trimethylaluminum; Imine; Amine.
INTRODUCTION

Over the years, Schiff base type compounds have primarily attracted attention due to their biological activity\textsuperscript{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 \textsuperscript{6-8}. Our interest in such systems stems from their potential to coordinate simultaneously multiple, catalytically active metal centers, and the potential ability to tune resulting cooperative effects. With this in mind, we have embarked upon a program to investigate structure/activity relationships during $\varepsilon$-caprolactone polymerization using macrocyclic Schiff base pro-catalysts bearing multiple main group centers \textsuperscript{9}. Our starting point is the simplest of this macrocyclic family, the so-called Robson-type macrocycles \textsuperscript{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 \textsuperscript{13-17}, however on occasion it has been possible to form the macrocycle in high yield in the absence of metal (and even acid catalyst) \textsuperscript{18,19}. Herein we show that use of the ethylene-bridged dianiline $[(\text{CH}_2\text{CH}_2)(2-\text{C}_6\text{H}_4\text{NH}_2)_2]$ and the dialdehyde [2-(OH)-5-(tBu)C\textsubscript{6}H\textsubscript{2}-1,3-(CHO)]\textsubscript{2} in refluxing toluene readily affords the [2+2] macrocyclic Schiff base 1, $\{[2-(OH)-5-(tBu)C\textsubscript{6}H\textsubscript{2}-1,3-CH][(\text{CH}_2\text{CH}_2)(2-C\textsubscript{6}H_4\textsubscript{NH})_2]\}_2$ in a template-free fashion. Furthermore, subsequent treatment with four equivalents of trimethylaluminum affords regiospecific methyl transfer yielding on hydrolysis the diimino-diamine macrocycle 2, $\{[2-(OH)-5-(tBu)C\textsubscript{6}H\textsubscript{2}-1-(CH)-3-C(\text{Me})H][(\text{CH}_2\text{CH}_2)(2-(N)-2'-C\textsubscript{6}H_4\text{NH})_2]\}_2$ in ca 74 % yield. Reaction of compound 1 with two equivalents of trimethylaluminum yields, after work-up, the tetraimino
supported dinuclear complex 3, \( \{(\text{Me}_2\text{Al})[\text{2-(O)-5-(tBu)}\text{C}_6\text{H}_2-1,3-(\text{CH})_2][\text{CH}_2\text{CH}_2][2-\text{C}_6\text{H}_4\text{N}\text{H}_2]_2 \} \), in good yield (ca 62%).

**EXPERIMENTAL SECTION**

**General**

No special precautions were used when preparing ligand 1. All manipulations involving Me₃Al were carried out under an atmosphere of dinitrogen using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glove-box. 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 400 S spectrometer at 400 MHz \( (^1\text{H}) \) or a Gemini 300 NMR spectrometer at 300 MHz \( (^1\text{H}) \). The \( ^1\text{H} \) 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 Perkin Elmer Spectrum BX FT-IR System equipped with an ATR probe.

**Materials**

2-hydroxy-5-tert-butyl-1,3-benzenedicarboxaldehyde \(^{20}\) and \( [(\text{CH}_2\text{CH}_2)(2-\text{C}_6\text{H}_4\text{NH}_2)_2] \) \(^{21}\) were prepared according to reported procedures. All other chemicals were obtained commercially and used as received unless stated otherwise.

**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 [(CH₂CH₂)(2-C₆H₄NH₂)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. Recrystallization from acetonitrile or toluene afforded 1 as pale yellow prisms (yield: 1.23 g, 82 %). ¹H NMR (CDCl₃, 400 MHz) δ 8.34 (br s, 4H, N=C(H)), 7.47-6.47 (m, 20H, Ar-H), 3.30 (br s, 8H, C(H₂)), 1.43 (s, 18H, C(CH₃)₃) ppm; elemental analysis calculated for C₅₂H₅₂N₄O₂: 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**

1 (1.00 g, 1.3 mmol) was dissolved in dry toluene (30 mL). Me₃Al (2M 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 removal of solvent, the resulting solid was washed with hot acetonitrile (dry) (3 x 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. Recrystallization from acetonitrile afforded 2 as pale yellow prisms (0.77 g, 74 %). ¹H
NMR (CDCl$_3$, 300 MHz) $\delta$ 8.56 (s, 2H, CH=N), 7.43 (s, 2H, C$_6$H$_2$), 7.27 (s, 2H, C$_6$H$_2$),
7.16 (pt, $J_{obs}$ = 7.7 Hz, 2H, CH=Np-C$_6$H$_4$), 7.01 (m, 4H, CH=No,m-C$_6$H$_4$), 6.93 (d, $J$ = 7.5 Hz, 2H, HNn-C$_6$H$_4$), 6.87 (pt, $J_{obs}$ = 7.5 Hz, 2H, HNn-C$_6$H$_4$), 6.69 (d, $J$ = 8.1 Hz, 2H, CH=N), 6.52 (pt, $J_{obs}$ = 7.4 Hz, 2H, HNp-C$_6$H$_4$), 6.26 (d, $J$ = 7.4 Hz, 2H, HNn-C$_6$H$_4$), 5.42 (d, $J$ = 10.3 Hz, 2H, NH), 4.73 (m, 2H, CH$_3$), 3.20 (d, $J$ = 9.8 Hz, 2H, C$_2$H$_2$), 3.09-2.88 (m, 4H, C$_2$H$_2$), 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

1 (1.00 g, 1.3 mmol) was dissolved in dry toluene (30 mL). Me$_3$Al (2M in hexanes) (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 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) $\delta$ 8.42 (d, $J$ = 2.5 Hz, 2H, C$_6$H$_2$), 8.14 (s, 2H, CH=N),
7.58 (d, $J$ = 7.7 Hz, 2H, AlN-$_o$-C$_6$H$_4$), 7.41 (pseudo t, $J$ = 7.7 Hz, 2H, AlN-m-C$_6$H$_4$), 7.24 (m, 2H, AlN-p-C$_6$H$_4$),
7.18 (pseudo t, $J$ = 7.5 Hz, 2H, N-m-C$_6$H$_4$), 7.02 (d, $J$ = 7.5 Hz, 2H, N-o-C$_6$H$_4$),
6.91 (d, $J$ = 2.5 Hz, 2H, C$_6$H$_2$), 6.88 (pseudo t, $J$ = 7.5 Hz, 2H, N-p-C$_6$H$_4$),
6.76 (d, $J$ = 7.8 Hz, 2H, AlN-m-C$_6$H$_4$), 6.50 (d, $J$ = 7.5 Hz, 2H, N-m-C$_6$H$_4$),
6.29 (s, 2H, CH=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 (t, $J_t$ = 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, AICH$_3$), -1.15 ppm (s, 6H, AICH$_3$); elemental analysis calculated for C$_{56}$H$_{62}$Al$_2$N$_4$O$_2$: 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$_7$H$_8$) on a Bruker-Nonius Roper CCD diffractometer, equipped with Mo-K$\alpha$ radiation [$\lambda$(Mo-K$\alpha$) = 0.71073 Å] and graphite monochromator. Intensity data were measured by thin-slice $\omega$- and $\varphi$-scans.

Data for 1 and 2.3(CH$_3$CN) were processed using the CrysAlis-CCD and -RED$^{22}$ programs, or, for 1.2(C$_7$H$_8$) 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 idealized 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$_3$CN), 1, and 1.2(C$_7$H$_8$) respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic
RESULTS AND DISCUSSION

Synthesis and Crystal Structures

The Schiff base macrocycle 1 (see Chart 1) is readily available in high yield (ca 82%) on refluxing (in toluene, for 24 h) the dianiline \([(\text{C}_2\text{H}_5\text{NH}_2)_2\text{]}\) and 2-hydroxy-5-tert-butyl-1,3-benzenedicarboxaldehyde \([2-(\text{OH})-5-(\text{tBu})\text{C}_6\text{H}_2-1,3-(\text{CHO})_2]\). The [2+2] condensation product 1 can be recrystallized from toluene as its toluene solvate (see Figure 1) or from acetonitrile as the solvent-free macrocycle (see Figure 2). Selected bond lengths and angles for both forms of 1 are presented in Table 1, with crystallographic parameters collated in Table 2.

![Chart 1](https://example.com/chart1.png)

**CHART 1** Schiff base macrocycles 1 and 2.
FIGURE 1  X-ray crystal structure of 1.2(C₇H₈) 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.

TABLE 1  Selected bond lengths and angles for 1.2(C\textsubscript{7}H\textsubscript{8}), 1 and 2.3(CH\textsubscript{3}CN) (Å, °)

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<th>1.2(C\textsubscript{7}H\textsubscript{8})</th>
<th>1</th>
<th>2.3(CH\textsubscript{3}CN)</th>
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<td>C(17)–N(18)</td>
<td>1.283(3)</td>
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<tr>
<td>N(18)–C(21)</td>
<td>1.417(3)</td>
<td>1.4206(17)</td>
<td>1.422(2)</td>
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<tr>
<td>N(37)–C(38)</td>
<td>1.277(3)</td>
<td>1.2554(17)</td>
<td>1.2863(19)</td>
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<tr>
<td>C(36)–N(37)</td>
<td>1.414(3)</td>
<td>1.4182(17)</td>
<td>1.4178(19)</td>
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<tr>
<td>C(16)–C(17)</td>
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<td>1.4514(18)</td>
<td>1.457(2)</td>
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<tr>
<td>C(12)–C(38′)</td>
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<td>1.4668(19)</td>
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<tr>
<td>C(46)–C(47)</td>
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<td>1.525(2)</td>
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<tr>
<td>C(12)–C(68)</td>
<td></td>
<td></td>
<td>1.518(2)</td>
</tr>
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<td>H(1)–N(18)</td>
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<td>1.71(2)</td>
<td>1.60(2)</td>
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<td>H(4)–N(37)</td>
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<td>1.75(2)</td>
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<tr>
<td>H(67)–O(1)</td>
<td></td>
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<td>2.37(2)</td>
</tr>
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</table>
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$_7$H$_8$) 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 structure of 1 and 1.2(C$_7$H$_8$). 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$_7$H$_8$) and 1 respectively).

Reaction of 1 with four equivalents of trimethylaluminum 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 aluminum to two imine moieties of the macrocycle to afford an intermediate dinuclear complex.
{(Me₂Al)[2-(O)-5-(tBu)C₆H₂-1-(CH)-3-C(Me)H][(CH₂CH₂)(2-(N)-2′-C₆H₄NH)₂]}₂

Such methyl transfers are now well established in α-diamine chemistry, and more recently for salicylaldimines, pyridylimines, pyridylbis(amine), and bis(imino)phenols. Crystals of 2 suitable for X-ray diffraction study were grown from a saturated acetonitrile solution at room temperature (see Figure 4). 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 trimethylaluminum did not give rise to methyl transfer to the imine moieties, but rather afforded the dinuclear complex {(Me₂Al)[2-(O)-5-(tBu)C₆H₂-1,3-(CH)₂][(CH₂CH₂)(2-C₆H₄)₂N]₂}₂ (3), as described in Figure 3. The structure of compound 3 was deduced from ¹H NMR spectroscopy, mass spectrometry and preliminary X-ray diffraction studies.

FIGURE 3  Compound 3
FIGURE 4  X-ray crystal structure of 2 in 2.3(CH$_3$CN) 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.

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 neighboring 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

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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 Me₃Al, namely
{(Me₂Al)[2-(O)-5-(tBu)C₆H₂-1,3-(CH)₂][(CH₂CH₂)(2-C₆H₄)₂N]₂}₂ reveals a clear
preference for the aluminum centers 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 triethylaluminum, Et₃Al, under similar conditions
affords the analogous ethylated macrocycle.⁹ We propose that this arrangement with the
aluminum centers ca 5.78 Å apart allows for a favorable interaction with the two
additional equivalents of Me₃Al that are required to bring about the methyl transfer to the
imine backbone. Interestingly, our preliminary screening of the ring opening
polymerization of ε-caprolactone using such organoaluminum-containing macrocycles,
has suggested there is a cooperative effect in operation when the aluminum centers are
predisposed as in 3.

TABLE 2  Crystal and structure refinement data for 1, 1.2(C₇H₈) and 2.3(CH₃CN)

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>1.2(C₇H₈)</th>
<th>2.3(CH₃CN)</th>
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<tr>
<td>Formula</td>
<td>C₅₂H₅₂N₄O₂</td>
<td>C₅₂H₅₂N₄O₂, 2(C₇H₈)</td>
<td>C₅₄H₆₀N₄O₂, 3(C₅H₄N)</td>
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<td>Formula weight</td>
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<td>920.2</td>
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<td>P₂₁/c (no. 14)</td>
<td>P-1 (no. 2)</td>
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<td>b (Å)</td>
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<td>20.5549(7)</td>
<td>14.3270(6)</td>
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<tr>
<td>c (Å)</td>
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<td>17.1484(6)</td>
<td>14.9271(6)</td>
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<tr>
<td>α (°)</td>
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<td>90</td>
<td>64.240(4)</td>
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</table>
$\beta (^\circ)\quad 91.693(3)\quad 101.485(2)\quad 82.897(3)$

$\gamma (^\circ)\quad 91.324(4)\quad 90\quad 82.141(3)$

$V (\text{Å}^3)\quad 1022.08(7)\quad 2702.99(15)\quad 2682.39(17)$

$Z\quad 1\quad 2\quad 2$

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 x 0.31 x 0.12 0.36 x 0.1 x 0.08 0.4 x 0.20 x 0.13

$\theta$(max) (°) 27.5 25.0 27.5

Reflexions measured 15129 16292 34729

Unique reflexions 4640 4728 12202

$R_{int}$ 0.051 0.060 0.060

Reflexions 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

**Spectroscopic and structural studies**

The neutral macrocyclic Schiff bases I–XV presented in Table 3 were used as comparison points in order to describe the structural and spectroscopic properties of compounds 1, 1.2(C$_7$H$_8$) and 2.3(CH$_3$CN). They all contain the same generic motif 1,3-(CHN)$_2$C$_5$H$_3$X (X = CH, C(OH), N) (Figure 5).

![Common motif of the macrocyclic Schiff base selected from the literature.](image-url)
For the bis(imino)phenol derivatives 1, 1.2(C\textsubscript{7}H\textsubscript{8}), 2.3(CH\textsubscript{3}CN) and I–IV, the C=N bond lengths are, in general, noticeably longer (from 1.2554(17) to 1.299(7) Å\textsuperscript{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\textsuperscript{33-35,39-43} and the bis(imino)benzyl (compounds VIII–X and XIV, from 1.254(7) to 1.274 Å\textsuperscript{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 length in both structures of 1 and in 2 are within the range of bond lengths reported for bis(imino)phenol based macrocyclic Schiff bases.\textsuperscript{18,44-47}

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

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

The cavity sizes measured for 1, 1.2(C\textsubscript{7}H\textsubscript{8}) and 2 (10.7 × 3.6 for 1 and 1.2(C\textsubscript{7}H\textsubscript{8}) and 6.5 × 4.3 Å for 2.3(CH\textsubscript{3}CN)) are somewhat smaller than that of compound I (16.0 × 5.8 Å),
another tetra-compartmental ligand based on a bis(imino)phenol moiety, which can accommodate two nickel metals in its cavity.\textsuperscript{46}

CONCLUSION

The template-free reaction of the dianiline \([(\text{CH}_3\text{CH}_2)(2-\text{C}_6\text{H}_4\text{NH}_2)_2]\) and 2-hydroxy-5-\text{tert}-butyl-1,3-benzenedicarboxaldehyde \([2-(\text{OH})-5-(\text{tBu})\text{C}_6\text{H}_2-1,3-(\text{CHO})]\) afforded the [2+2] macrocyclic Schiff base ligand 1 in excellent yield. Treatment of 1 with four equivalents of Me\textsubscript{3}Al and subsequent hydrolysis afforded the imino/amino compound 2, in good yield, through a regioselective methyl transfer at aluminum. Similar treatment of 1 with two equivalents of Me\textsubscript{3}Al afforded the dinuclear complex 3 in good yield. Compounds 1 and 2 are tetra-compartmental 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 polymerization will be reported shortly.

Acknowledgements

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References


(25) Arbaou, A.; Redshaw, C.; Hughes, D. L., *The crystal structure of this complex will be reported elsewhere.*


CHART 1 Schiff base macrocycles 1 and 2.
157x60mm (600 x 600 DPI)
$X = 1,2$-$C_{6}H_{10}$ III $X = CH(C_{6}H_{5})CH(C_{6}H_{5})$ IV

$R_{1} = R_{2} = H, X = 1,2$-$C_{6}H_{10}$ V

$R_{1} = CH_{3}, R_{2} = H, X = 1,2$-$C_{6}H_{10}$ VI

$R = CH_{3}, X = 1,2$-$C_{6}H_{10}$ VII

$R = fBu, X = 1,3$-(CH$_{2}$)$_{2}$C$_{6}$H$_{4}$ X

$X = CH$ XIV

$X = N$ XV
FIGURE 3 Compound 3

77x47mm (600 x 600 DPI)
FIGURE 4 X-ray crystal structure of 2 in 2.3(CH$_3$CN) 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.

159x198mm (600 x 600 DPI)
FIGURE 5 Common motif of the macrocyclic Schiff base selected from the literature.

X = CH, C(OH) and N