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The synthesis of small azamacrocycles bearing pendant aromatic functionalities. The crystal structures of $[Cu(L_1)_2](PF_6)_2$, $[(L_1)CuCl_2]$, $[Cu(L_6)(NO_3)_2]$ and $[Cu_2(L_7-H)_2(OH_2)_2](PF_6)_2 \cdot 3H_2O$ $(L_1 = N-(mesitylethyl)-1,4,7-triazacyclononane,$ $L_6 = N-(4-hydroxymethylbenzyl)-1,4,7-triazacylcononane,$ $L_7 = N-(4-benzylcarboxylic acid)-1,4,7-triazacylcononane)$

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Abstract

A simple synthetic procedure for the mono- or di-functionalization of tri- and tetra-azamacrocycles with electron rich arenes has been developed. Specifically, 1,4,7-triazacyclononane (tacn), 1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,8,11-tetraazacyclote-tradecane (cyclam) react with 2,4,6-trimethylstyrene in the presence of *n*-butyllithium to give, respectively *N*-(mesitylethyl)-1,4,7-triazacyclononane (\mathbf{L}_1), *N*-(mesitylethyl)-1,4,7,10-tetraazacyclododecane (\mathbf{L}_4), and *N*-(mesitylethyl)-1,4,8,11-tetraazacyclo-tetradecane (\mathbf{L}_5). In contrast, when styrene itself or *p*-vinylanisole are used as the Michael acceptor with 1,4,7-triazacyclononane, the *N'*,*N"* product is formed, respectively *N'*,*N"-bis*(phenylethyl)-1,4,7-triazacyclononane (\mathbf{L}_2) and *N'*,*N"-bis*(*p*-methoxyphenyl-ethyl)-1,4,7-triazacyclononane (\mathbf{L}_3). Using conventional mono-functionalization techniques, the phenyl derivatives *N*-(4-hydroxymethylbenzyl)-1,4,7-triazacyclononane (\mathbf{L}_6) and *N*-(4-benzylcarboxylic acid)-1,4,7-triazacyclononane (\mathbf{L}_7) have also been synthesised. A series of transition metal complexes of \mathbf{L}_1 to \mathbf{L}_7 with Ni(II), Cu(II), Zn(II) and Co(II) have been prepared. The X-ray crystal structures of [Cu(\mathbf{L}_1)₂[(PF₆)₂, [(\mathbf{L}_1)CuCl₂], [Cu(\mathbf{L}_6)(NO₃)₂] and [Cu₂(\mathbf{L}_7 -H)₂(OH₂)₂](PF₆)₂·3H₂O are described. In all of these complexes, coordination to the metal takes place through the macrocycle nitrogens. The crystal structure of [Cu₂(\mathbf{L}_7 -H)₂(OH₂)₂](PF₆)₂·3H₂O reveals that it is a coordinate-polymeric material. Attempts to coordinate the pendent arenes to Rh(I) are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Azamacrocycles; Aromatic pendant arms; Coordination compounds; Metallic polymer

1. Introduction

The chemistry of triazamacrocycles, *N*-functionalized with hard ligators, e.g. carboxylic acids [1], alcohols [2], amines [3], sulfates [4], phosphates [5], imidazoles [6]

and pyridine [7] is now well established. More recently the chemistry has been extended to include more classic soft donors such as sulfides [8], alkenes [9], phosphines [10] and alkynes [11]. As part of our own research effort we have been exploring the possibility of introducing aromatic groups onto the macrocycle (Scheme 1), which are either electron rich so as to generate organometallic clusters, or have oxygen binding sites for further molecular recognition [12]. As a result we

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Scheme 1. List and numbering scheme of the macrocycles discussed in the text.

now present some of our work towards these goals. In particular, a high yielding procedure is reported for the monofunctionalization of tacn with the electron rich arene derived from 2,4,6-trimethylstyrene.

Syntheses of single pendent arm macrocycles are comparatively rare, and are often not straightforward, requiring chromatographic separation of the products. We have found that direct reaction of an excess of 2,4,6-trimethylstyrene with either of the macrocycles, tacn, cyclen or cyclam in the presence of *n*-butyllithium leads to good yields of the monosubstituted products without further separation. Under the same experimental conditions, the vinylaromatics styrene or *p*-vinylanisole give the N',N'' disubstituted products, in a similarly pure state.

Complexes of L_1 with the metals, Cu(II), Ni(II), Co(II) and Zn(II) were synthesised and the X-ray crystal structures of $[Cu(L_1)_2](PF_6)_2$ and $[(L_1)CuCl_2]$ are described. It was anticipated that the pendent 'acti-



Scheme 2. Pictorial representation of potential products from the self-assembly of an 'L' type motif.

vated' arene of the coordinated ligand would react with soft metal centres, but no reaction was observed with Rh(I) [13] or Mo(0) [14] despite the use of forcing conditions. Complexes of L_6 with the metals, Cu(II), Ni(II), Co(II) and L_7 with Cu(II) were also prepared. In these two cases it was expected that the hydroxyl or carboxyl unit would play host to intermolecular bonding, and hence the construction of self-assembled molecular aggregates (e.g. polymers, boxes) as illustrated in Scheme 2.

2. Experimental

All chemicals unless otherwise stated were purchased from Aldrich and used as received. 1,4,7,10-Tetraazacyclododecane (cyclen) was purchased from Strem Chemicals. Solvents where necessary were dried by reported methods [15]. 1,4,7-Triazacyclononane (tacn) [16], 1,4,8,11-tetraazacyclotetradecane (cyclam) [17], 1,4,7triazacyclo[5.2.1.^{04.10}]decane [18] and [Rh(μ-Cl)(COD)]₂ [19] were synthesised according to literature procedures. ¹H and ¹³C NMR spectra were recorded using a Bruker AM360 360 MHz spectrometer. UV–Vis spectra were recorded using a Shimadzu UV-3101 PC spectrophotometer. Mass spectra were obtained using a JEOL JMS 700 (The MStation) mass spectrometer. Combustion analysis was performed using in-house facilities.

2.1. Synthesis of N-(mesitylethyl)-1,4,7triazacyclononane (L_1)

"BuLi (4 ml of a 2.5 M solution in hexanes, 10 mmol) was added dropwise to a solution of tacn (1.0 g, 7.8 mmol) dissolved in THF (20 ml). The reaction mix was stirred for 5 min, followed by the dropwise addition of 2,4,6-trimethylstyrene (3.4 g, 23.2 mmol) in THF (10 ml) and the solution stirred at 60 °C for 16 h. Water (1 ml) was added and the reaction mix stirred for 5 min. All volatiles were removed in vacuo. The residue was extracted into CH₂Cl₂ and the solution extracted with 2 M HCl $(2 \times 40 \text{ ml})$. The aq. phase was basified with NaOH (1 M) solution and the free ligand extracted into $CHCl_3$ (3 × 40 ml). The combined organic phases were dried over MgSO₄, filtered and the solvents removed in vacuo to leave a clear oil which slowly solidified. Yield: 1.1 g, 3.9 mmol, 50%. ¹H NMR (CDCl₃): $\delta = 6.80$ (s, 2H, $C_6H_2Me_3$), 2.98–2.60 (m, 18H, CH_2NH), 2.27 (s, 6H, $o-C_6H_2(CH_3)_2$, 2.21 (s, 3H, $p-C_6H_2CH_3$). ¹³C NMR (CDCl₃): $\delta = 136.0$, 135.3, 133.3, 128.9 (phenyl-C), 55.6 (N-CH₂-CH₂-C $_{6}$ H₂Me₃), 52.3, 46.7, 46.4 (N-CH₂-CH₂-N), 27.2 (N-CH₂-CH₂-C₆H₂Me₃), 20.8 $(p-C_6H_2CH_3)$, 19.8 $(o-C_6H_2(CH_3)_2)$. EI MS: m/ $z = 273 [M - 2H]^+, 154 [M - C_6H_2Me_3]^+.$

2.2. Synthesis of N-(mesitylethyl)-1,4,7,10tetraazacyclododecane (L_4)

"BuLi (1.6 ml of a 2.5 M solution in hexanes, 4.0 mmol) was added dropwise to a solution of cyclen (0.50 g, 3.0 mmol) in THF (20 ml). The reaction mixture was stirred for 5 min, followed by the addition of 2,4,6trimethylstyrene (1.3 g, 9 mmol) in THF (10 ml) and the reaction mixture was stirred at 60 °C for 16 h. Water (5 ml) was added and the reaction mixture stirred for 5 min. All volatiles were removed in vacuo. The residue was dissolved in CH₂Cl₂ and the solution extracted into 2 M HCl (2×40 ml). The aq. phase was basified with NaOH (1 M) solution and the free ligand extracted into $CHCl_3$ (3 × 40 ml). The combined organic phases were dried over MgSO₄, filtered and the solvents removed in vacuo to leave a clear, yellow oil. Yield: 0.58 g, 1.8 mmol, 60%. ¹H NMR (CDCl₃): $\delta = 6.80$ (s, 2H, C₆H₂Me₃), 2.82–2.50 (m, 23H, CH₂,NH), 2.27 (s, 6H, o-C₆H₂(CH₃)₂), 2.21 (s, 3H, $p-C_6H_2CH_3$). ¹³C NMR (CDCl₃): $\delta = 135.9$, 135.0, 133.2, 129.7 (phenyl-*C*), 53.0 (N-*C*H₂-CH₂-C₆H₂Me₃), 51.0, 46.9, 45.7, 45.3 (N-CH₂-CH₂-N), 26.8 (N-CH₂- $CH_2-C_6H_2Me_3$), 20.6 ($p-C_6H_2CH_3$), 19.5 ($o-C_6H_2-CH_3$) $(CH_3)_2$). EI MS: $m/z = 185 [M - (CH_2)_2C_6 - H_2Me_3]^+$, 147 $[(CH_2)_2C_6H_2Me_3]^+$, 133 $[CH_2C_6H_2Me_3]^+$.

2.3. Synthesis of N-(mesitylethyl)-1,4,8,11-tetraazacyclotetradecane (L_5)

Prepared similarly to L₁ from cyclam (0.40 g, 2.0 mmol), "BuLi (1.1 ml of a 2.5 M solution in hexanes, 2.8 mmol) and 2,4,6-trimethylstyrene (1.2 g, 8.0 mmol). Yield: 0.30 g, 0.88 mmol, 44%. ¹H NMR (CDCl₃): $\delta = 6.73$ (s, 2H, C₆H₂Me₃), 2.72–2.51 (m, 23H, NH, N–CH₂–CH₂–N,N–CH₂–CH₂–CH₂–N), 2.23 (s, 6H, *o*-C₆H₂(CH₃)₂), 2.15 (s, 3H, *p*-C₆H₂CH₃), 1.67 (m, 4H, N–CH₂–CH₂–C₆H₂Me₃). ¹³C NMR (CDCl₃): $\delta = 135.9$, 134.8, 133.4, 128.7 (phenyl–C), 54.0, 52.3, 50.9, 50.7, 50.5, 49.3, 49.1, 49.0, 48.9, 47.9, 28.9, 28.6, 26.3, 24.5 (CH₂), 20.7 (*p*-C₆H₂CH₃), 19.8 (*o*-C₆H₂(CH₃)₂). EI MS: *m*/*z* = 213 [*M* – CH₂(C₆H₂Me₃]⁺, 147 [(CH₂)₂C₆-H₂Me₃]⁺.

2.4. Synthesis of N', N''-bis(phenylethyl)-1,4,7triazacyclononane (L_2)

Prepared similarly to L_1 from tacn (0.20 g, 1.58 mmol), "BuLi (1.0 ml of a 2.5 M solution in hexanes, 2.1 mmol) and styrene (0.50 g, 4.8 mmol). Yield: 0.24 g, 0.72 mmol, 45%. ¹H NMR (CDCl₃): $\delta = 7.29-7.18$ (m, 10H, C₆H₅), 2.79-2.62 (21H, CH₂ NH). ¹³C NMR (CDCl₃): $\delta = 140.6$, 128.6, 128.3, 125.9 (phenyl-*C*), 59.1 (NH-CH₂-CH₂-C₆H₅), 53.0, 53.5, 46.7 (NH-CH₂-CH₂-NH), 34.1 (NH-CH₂-CH₂-C₆H₅). EI

MS: $m/z = 335 [M]^+$, 246 $[M - CH_2C_6H_5]^+$, 105 $[C_6H_5(CH_2)_2]^+$.

2.5. Synthesis of N',N"-bis(p-methoxyphenylethyl)-1,4,7-triazacyclononane (L_3)

Prepared similarly to L_1 from tacn (0.21 g, 1.58 mmol), "BuLi (1.0 ml of a 2.5 M solution in hexanes, 2.1 mmol), and *p*-vinylanisole (0.64 g, 4.8 mmol). Yield: 0.28 g, 0.71 mmol, 45%. ¹H NMR (CDCl₃): $\delta = 7.09$ (d, 4H, C₆H₄, J = 8.64 Hz), 6.81 (d, 4H, C₆H₄, J = 8.68 Hz), 3.74 (s, 6H, CH₃), 2.71–2.58 (m, 21H, CH₂, NH). ¹³C NMR (CDCl₃): 157.8, 132.2, 129.6, 113.7 (phenyl–*C*), 59.0 (N–CH₂–CH₂–C₆H₄OMe), 55.1 (CH₃), 52.3, 50.1, 45.8 (N–CH₂–CH₂–N), 33.0 (N–CH₂–CH₂–C₆H₄OMe]- EI MS: m/z = 396 [M]⁺, 276 [M – CH₂C₆H₄OMe]⁺, 135 [CH₂CH₂C₆H₄OMe]⁺.

2.5.1. Synthesis of A

To a one-necked flask flushed with dinitrogen and charged with 1,4,7-triazacyclo[5.2.1.^{04,10}]decane (0.69 g, 4.96 mmol) in dry THF (30 ml), was slowly added 4-bromomethylbenzyl alcohol (1 g, 4.98 mmol) in dry THF (20 ml). The reaction mixture was stirred overnight and the resultant white precipitate filtered washed with THF and dried. Yield: 1.03 g, 3.02 mmol, 61%. ¹H NMR (C₃H₆O-d₆): $\delta = 7.73-7.72$ (d, 2H, C₆H₄, J = 7.9 Hz), 7.54–7.52 (d, 2H, C6H₄, J = 7.9 Hz), 5.97 (s, 1H, N–CH), 4.75 (s, 2H, Ar–CH₂), 4.71 (s, 2H, ArCH₂), 3.50–3.42 (m, 2H, N–CH₂), 3.33–3.25 (m, 4H, N–CH₂).

2.6. Synthesis of N-(4-hydroxymethylbenzyl)-1,4,7triazacyclononane (L_6)

Compound A (1.31 g, 3.85 mmol) was refluxed in water (40 ml) for 4 h followed by the addition of NaOH (0.54 g, 10 mmol). The resulting basic solution was refluxed for 24 h and the water removed with $C_6H_5CH_3$ using a Dean–Stark apparatus. Removal of the $C_6H_5CH_3$ afforded an oil which was sufficiently pure enough for metal ion complexation. Yield: 0.65 g, 2.6 mmol, 68%. ¹H NMR (CDCl₃): $\delta = 7.26$ (s, 4H, C_6H_4), 4.53 (s, 2H, N– CH_2 –OH), 3.62 (s, 2H, CH_2 –N), 2.65 (m, 4H, N– CH_2), 2.54 (m, 8H, N– CH_2). EI MS: $m/z = 250 [MH]^+$.

2.6.1. Synthesis of **B**

This compound was prepared in a similar manner to that reported for compound **A**, using methyl-4-(bromomethyl)benzoate (1 g, 4.37 mmol) and 1,4,7-triazacyclo[5.2.1.^{04.10}]decane (0.69 g, 4.96 mmol). Yield: 1.1 g, 2.98 mmol, 68%. ¹H NMR (C₃H₆O-d₆): $\delta = 8.11-8.09$ (d, 2H, C₆H₄, J = 8.1 Hz), 7.91–7.88 (d, 2H, C₆H₄, J = 8.2 Hz), 6.02 (s, 1H, NCH), 4.79 (s, 2H, Ar–CH₂), 3.98–3.93 (m, 2H, NCH₂), 3.90 (s, 3H, OCH₃), 3.82–3.75 (m, 4H, N–CH₂), 3.45–3.32 (m, 2H, NCH₂), 3.26–3.31 (q, 4H, NCH₂, J = 6.7 Hz).

2.7. Synthesis of N-(4-benzylcarboxylic acid)-1,4,7-triazacyclononane (L_7)

Compound B (1 g, 2.8 mmol) was dissolved in water (50 ml) and refluxed for 2 h followed by addition of NaOH (0.2 g, 5 mmol) and further refluxing for 4 h. The solution was cooled to room temperature and extracted with CH₂Cl₂ to remove organic impurities. The solution was made acidic with concd. HBr and the solvent removed on a rotary evaporator. The remaining solid was extracted with EtOH $(3 \times 50 \text{ cm}^3)$ and the combined EtOH fractions removes on a rotary evaporator to afford a yellow solid, which was recrystallized from MeOH-Et₂O (1:5). Yield: 0.44 g, 1.7 mmol, 60%. ¹H NMR (DMSO- d_6): $\delta = 7.91 - 7.88$ (d, 2H, C₆ H_4 , J = 8.0 Hz), 7.57–7.54 (d, 2H, C₆ H_4 , J = 8.1 Hz), 4.42 (s, 2H, Ar-CH₂), 3.88 (m, 4H, N-CH₂), 3.13 (m, 4H, N–CH₂), 2.87 (m, 4H, N–CH₂). EI MS: m/z = 264 $[MH]^+$, 247 $[M - OH]^+$, 219 $[M - CO_2H]^+$.

2.8. Metal complexes

2.8.1. $[Cu(L_1)_2](PF_6)_2 \cdot 1/2CH_3CN$ (1)

The ligand L₁ (150 mg, 0.55 mmol) in EtOH (2 ml) was added to CuCl₂·2H₂O (48 mg, 0.28 mmol) in EtOH (10 ml), containing NH₄PF₆ (230 mg). Stirring was continued for approximately 16 h. A blue precipitate was filtered off, washed with EtOH and ether, and air-dried. The compound was recrystallized from MeCN. Yield: 138 mg (50%). IR (cm⁻¹): 3142 $v_{(N-H)}$, 843 $v_{(P-F)}$. CHN Found (Calc.): C, 45.80 (45.45); H, 6.55 (6.48); N, 9.46 (9.84)%.

2.8.2. $[Co(L_1)_2](PF_6)_2$ (2)

The ligand L_1 (256 mg, 0.93 mmol) in EtOH (5 ml) was added to CoCl₂·6H₂O (88 mg, 0.37 mmol) in degassed EtOH (20 ml), containing NH₄PF₆ (300 mg). The reaction mixture was stirred for approximately 16 h under nitrogen. A pink precipitate was filtered off, washed repeatedly with EtOH and dried in vacuo. Yield: 200 mg (60%). IR (cm⁻¹): 3200 $v_{(N-H)}$, 845 $v_{(P-F)}$. CHN Found (Calc.): C, 45.30 (45.39); H, 6.57 (6.50); N, 9.18 (9.34)%.

2.8.3. $[Zn(L_1)_2](PF_6)_2$ (3)

The ligand L_1 (200 mg, 0.72 mmol) in EtOH (2 ml) was added to ZnCl₂ (48 mg, 0.36 mmol) in EtOH (20 ml) containing NH₄PF₆ (300 mg). The mixture was stirred for 2 h. A white precipitate was then filtered off, washed with EtOH and dried in vacuo. Yield: 183 mg (56%). IR (cm⁻¹): 3214 $v_{(N-H)}$, 843 $v_{(P-F)}$. CHN Found

(Calc.): C, 44.9 (45.06); H, 6.52 (6.45); N, 9.23 (9.27)%. ¹H NMR (CD₃CN): $\delta = 6.87$ (s, 4H, phenyl–*H*), 3.31 (s, 4H, N*H*), 2.96–2.64 (m, 32H, C*H*₂), 2.25 (s, 12H, o-C₆H₂(C*H*₃)₂), 2.23 (s, 6H, *p*-C₆H₂C*H*₃). ¹³C NMR (CD₃CN): 136.8, 131.6, 129.5, 117.8 (phenyl–*C*), 55.8, 49.1, 44.0, 43.2 (N–CH₂), 22.5 (CH₂-mesityl), 20.3 (*p*-C₆H₂CH₃), 19.5 (*o*-C₆H₂(CH₃)₂).

2.8.4. $[Ni(L_1)_2](PF_6)_2$ (4)

The ligand L₁ (150 mg, 0.55 mmol) in EtOH (5 ml) was added to NiCl₂·6H₂O (60 mg, 0.25 mmol) in EtOH (20 ml), containing NH₄PF₆ (200 mg). The mixture was stirred for 4 h. A purple precipitate was filtered off and air-dried. Yield: 100 mg (44%). IR (cm⁻¹): 3270 $v_{(N-H)}$, 841 $v_{(P-F)}$. CHN Found (Calc.): C, 44.9 (45.4); H, 6.71 (6.50); N, 8.88 (9.34)%.

2.8.5. $[Cu(L_4)](ClO_4)_2 \cdot 1/2EtOH$ (5)

The ligand L_4 (140 mg, 0.44 mmol) in EtOH (5 ml) was added to Cu(ClO₄)₂·6H₂O (130 mg, 0.35 mmol) in EtOH (20 ml). The solution was stirred for 24 h. A purple precipitate was filtered off, washed with EtOH and dried in vacuo. Yield: 114 mg (54%). IR (cm⁻¹): 3280 $\nu_{(N-H)}$, 1100 $\nu_{(Cl-O)}$. CHN Found (Calc.): C, 40.0 (39.77); H, 5.78 (6.17); N, 8.95 (9.28)%. UV–Vis (CH₃NO₂): λ_{max} (nm) (ε_{max} , mol⁻¹ 1 cm⁻¹): 579 (334).

2.8.6. $[Zn(L_4)Cl](ClO_4)_2$ (6)

The ligand L_4 (202 mg, 0.64 mmol) in EtOH (3 ml) was added to ZnCl₂ (69 mg, 0.51 mmol) in EtOH (20 ml) containing LiClO₄ (300 mg). Stirring was continued for approximately 24 h. The white precipitate was filtered off, washed with EtOH and ether and dried in vacuo. Yield: 120 mg (45%). ¹H NMR (CD₃CN): δ = 6.84 (s, 2H, phenyl–*H*), 3.11–2.69 (m, 23H, C*H*₂ N*H*), 2.27 (s, 6H, *o*-C₆H₂(C*H*₃)₂), 2.20 (s, 3H, *p*-C₆H₂C*H*₃). ¹³C NMR (CD₃CN): 137.2, 132.8, 130.0, 118.3 (phenyl–*C*), 53.0 (N–CH₂–CH₂–mes), 50.2, 45.5, 44.6, 43.6 (N–CH₂–CH₂–N), 22.5 (CH₂–mes), 20.9 (*p*-C₆H₂CH₃), 19.9 (*o*-C₆H₂(CH₃)₂). IR (cm⁻¹): 3280 $v_{(N-H)}$, 1090 $v_{(Cl-O)}$. CHN Found (Calc.): C, 44.1 (44.6); H, 6.74 (6.71); N, 10.2 (10.9)%.

2.8.7. $[Ni(L_4)](ClO_4)_2 \cdot 1/2Et_2O$ (7)

The ligand L₄ (301 mg, 0.94 mmol) in butan-1-ol (10 ml) was added to Ni(ClO₄)₂·6H₂O (278 mg, 0.76 mmol) in hot butan-1-ol (30 ml). The reaction mixture was stirred for 24 h. A green precipitate was filtered off, washed with butan-1-ol and dried in vacuo. Yield: 142 mg. The blue liquor was concentrated in vacuo to dryness to leave a yellow solid. This was washed repeatedly with ether and dried in vacuo. Yield: 280 mg (64%). IR (cm⁻¹): 3260 $\nu_{(N-H)}$, 1100 $\nu_{(Cl-O)}$. CHN Found (Calc.): C, 40.60 (41.14); H, 6.19 (6.41); N, 8.54 (9.14)%. UV–Vis (CH₃NO₂): λ_{max} (nm) (ε_{max} , mol⁻¹ 1 cm⁻¹): 418 (40), 454 (26.1), 878 (27.9).

2.8.8. $[Cu(L_5)](ClO_4)_2 \cdot H_2O(8)$

The ligand L_5 (120 mg, 0.34 mmol) in EtOH (2 ml) was added to Cu(ClO₄)₂·6H₂O (100 mg, 0.27 mmol) in EtOH (10 ml). The reaction mixture was stirred for approximately 16 h. A purple precipitate was filtered off, washed with EtOH and ether, and dried in vacuo. Yield: 105 mg (63%). IR (cm⁻¹): 3230 $v_{(N-H)}$, 1100 $v_{(Cl-O)}$. CHN Found (Calc.): C, 40.7 (40.23); H, 6.38 (6.43); N, 9.33 (8.94)%. UV–Vis (MeOH): λ_{max} (nm) (ε_{max} , mol⁻¹ 1 cm⁻¹): 516 (135).

2.8.9. $[Ni(L_5)](ClO_4)_2$ (9)

The ligand L_5 (150 mg, 0.43 mmol) in EtOH (5 ml) was added to Ni(ClO₄)₂·6H₂O (124 mg, 0.34 mmol) in EtOH (20 ml). The reaction mixture was stirred for approximately 16 h. A red precipitate was filtered off, washed with EtOH and ether, and dried in vacuo. Yield: 98 mg (50%). IR (cm⁻¹): 3210 $\nu_{(N-H)}$, 1100 $\nu_{(Cl-O)}$. CHN Found (Calc.): C, 41.3 (41.7); H, 6.24 (6.35); N, 9.28 (9.28)%. UV–Vis (MeOH): λ_{max} (nm) (ε_{max} , mol⁻¹ 1 cm⁻¹): 463.5 (79).

2.8.10. $[Ni(L_5)Cl_2]$ (10)

(a) The ligand L_5 (150 mg, 0.43 mmol) in EtOH (5 ml) was added to NiCl₂·6H₂O (93 mg, 0.39 mmol) in warm EtOH (20 ml). The reaction mixture was stirred for approximately 16 h. Diethyl ether was added and a mauve precipitate was filtered off, washed with ether and dried in vacuo. Yield: 23 mg (12%).

(b) LiCl (108 mg, 2.55 mmol) in C_3H_6O (10 ml) was added to **9** (150 mg, 0.207 mmol) in C_3H_6O (10 ml) with stirring. A mauve precipitate was filtered off, washed with C_3H_6O , and dried in vacuo. Yield: 23 mg (15%). IR (cm⁻¹): 3190 $\nu_{(N-H)}$. CHN Found (Calc.): C, 52.9 (53.0); H, 7.99 (8.06); N, 11.57 (11.77)%. UV–Vis (MeOH): λ_{max} (nm) (ε_{max} , mol⁻¹ 1 cm⁻¹): 463 (90).

2.8.11. Reaction of L_1 with $[Rh(COD)]^+(PF_6)^-$

AgPF₆ (101 mg, 0.40 mmol) in MeCN (5 ml) was added under nitrogen to $[Rh(\mu-Cl)(COD)]_2$ (100 mg, 0.20 mmol) in MeCN (10 ml). The yellow solution was separated from precipitated AgCl and added to **6** (362 mg, 0.40 mmol) in MeCN (10 ml). No reaction was observed by ¹H or ¹³C NMR spectroscopy after prolonged heating and stirring. When **6** was substituted by free L₁, no reaction of the pendent arene group was observed.

2.8.12. $[Ni(L_6)_2](PF_6)_2$ (12)

The ligand L_6 (200 mg, 0.8 mmol) in EtOH (5 ml) was added to a solution of Ni(NO₃)₂·6H₂O (0.23 g, 0.79 mmol) in H₂O (5 ml) and stirred for 5 min. A saturated NH₄PF₆ solution was added and the product extracted with CH₃NO₂ (2 × 5 ml). The or-

ganic layer was separated and removed to give oil, which was recrystallized from CH₃CN-Et₂O (1:3). Yield: 100 mg (30%). IR (cm⁻¹): 3424 $v_{(N-H)}$, 2927 $v_{(C-H)}$, 843 $v_{(P-F)}$. FAB MS: m/z = 701 [Ni(L₆)₂](PF₆)⁺, 555 [Ni(L₆)₂]⁺. UV-Vis (CH₃CN): λ_{max} (nm) (ε_{max} , mol⁻¹ l cm⁻¹): 885 (18), 533 (10), 316 (63).

2.8.13. $[Co(L_6)(NO_3)_2(OH_2)] \cdot H_2O$ (13)

The ligand L_6 (100 mg, 0.4 mmol) in EtOH (5 ml) was added to a solution of Co(NO₃)₂·6H₂O (116 mg, 0.4 mmol) in H₂O (5 ml) and stirred for 5 min. The solution was left to slowly evaporate until a precipitate formed, which was filtered off and purified by passing down a Sephadex column eluting with CH₃CN. Yield: 69 mg (40%). IR (cm⁻¹): 3527 v_{OH} , 3272 v_{NH} , 1480, 1318 v_{NO_2} . FAB MS: m/z = 370 [Co(L₆)NO₃]⁺. CHN Found (Calc.): C, 37.10 (37.34); H, 5.85 (5.60); N, 15.08 (15.55)%. UV–Vis (CH₃CN): λ_{max} (nm) (ε_{max} , mol⁻¹ 1 cm⁻¹): 539 (119).

2.8.14. $[Cu(L_6)(NO_3)_2]$ (14)

The ligand L_6 (97 mg, 0.39 mmol) in EtOH (5 ml) was added to a solution of Cu(NO₃)₂·3H₂O (94 mg, 0.39 mmol) in H₂O (5 ml) and stirred for 5 min. The solution was left to slowly evaporate until a precipitate was formed, which was filtered off and purified as described above. Yield: 85 mg (50%). IR (cm⁻¹): 3527 v_{OH} , 3272 v_{NH} , 1480, 1318 v_{NO_2} . FAB MS: m/z = 374 [Cu(L₆)NO₃]⁺. CHN Found (Calc.): C, 38.68 (38.48); H, 5.36 (5.31); N, 15.87 (16.03)%. UV–Vis (CH₃CN): λ_{max} (nm) (ε_{max} , mol⁻¹ 1 cm⁻¹): 647 (59).

2.8.15. $[Cu(L_7)(Br_2)] \cdot 2H_2O$ (15)

The ligand L_7 ·HBr (158 mg, 0.46 mmol) in H₂O (5 ml) was added to a solution of Cu(NO₃)₂·3H₂O (111 mg, 0.46 mmol) in H₂O (5 ml) and stirred for 5 min. The solution was left to slowly evaporate until a precipitate formed, which was filtered off and dried under vacuum. Yield: 89 mg (37%). IR (cm⁻¹): 3430 $v_{\rm OH}$, 3288 $v_{\rm NH}$, 2920 $v_{\rm CH}$, 1695 $v_{\rm CO}$. FAB MS: $m/z = 485 \ [Cu(L_7)Br_2]^+$, 407 $[Cu(L_7)Br]^+$, 326 $[Cu(L_7)]^+$. CHN Found (Calc.): C, 31.79 (32.16); H, 4.12 (4.82); N, 8.55 (8.04)%. UV–Vis (H₂O): $\lambda_{\rm max}$ (nm) ($\varepsilon_{\rm max}$, mol⁻¹ 1 cm⁻¹): 650 (39).

2.8.16. $[Cu_2(L_7-H)_2(OH_2)_2](PF_6)_2 \cdot 6H_2O$ (16)

A saturated aq. solution of KPF₆ was added to a solution of $[Cu(L_7)(Br_2)] \cdot 2H_2O$ (40 mg, 0.076 mmol) in H₂O (5 ml). The water was allowed to slowly evaporate until a blue crystalline solid precipitated, which was filtered off and dried under vacuum. Yield: 37 mg (95%). IR (cm⁻¹): 3430 v_{OH}, 2925 v_{CH}, 1609 v_{CO}, 838 v_{PF}. CHN Found (Calc.): C, 30.36 (30.96); H, 4.03 (4.79); N, 7.33 (7.74)%. FAB MS: m/z = 326 $[Cu(L_7)]^+$.

2.9. Crystallography

Details of the data collection and analysis of 1, 14 and 16 are collected in Table 1. Single crystals were attached to a glass fibre using acrylic resin, and mounted on a goniometer head in a general position. Data were collected using an Enraf-Nonius CAD4 diffractometer (compound 1) or a Bruker-Nonius Kappa CCD diffractometer (compounds 14 and 16) graphite-monochromated X-radiation ($\lambda =$ using 0.71073 Å). The structures were solved by direct methods (SIR-92) [20]. All non-H atoms were allowed anisotropic thermal motion. Aliphatic CH hydrogen atoms were included at calculated positions with C-H = 0.96 Å. Refinement (SHELXL-97) [21] was by full-matrix least-squares on F^2 . All crystals of 16, which were examined proved to be twins. The crystal chosen was twinned according to a rotation of 180° about 010. Many reflections from both lattices are overlapped. Despite these problems, the overall identity of compound 16 was satisfactorily determined by the X-ray analysis. Neutral atom scattering factors, coefficients and anomalous dispersion and absorption coefficients were obtained from [22].

3. Results and discussion

3.1. Synthesis of the ligands

The ligands L_1-L_5 were synthesised according to a

Table 1	
Crystallographic	data

Compound	1	14	16
Chemical	C ₆₈ H ₁₁₆ Cl ₄ Cu ₃ -	C ₁₄ H ₂₃ CuN ₅ -	$C_{28}H_{50}N_6Cu_2O_9$
formula	$F_{12}N_{12}P_2$	O_7	P_2F_{12}
Formula weight	1724.09	436.91	1031.76
Temperature (°C)	291	-123	-173
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
Crystal system	triclinic	triclinic	triclinic
a (Å)	11.834(2)	7.3210(2)	10.2057(1)
b (Å)	13.114(3)	8.2780(2)	12.8715(2)
c (Å)	13.581(3)	16.3904(6)	16.6340(3)
α (°)	75.556(19)	80.800(1)	72.597(1)
β (°)	84.126(17)	89.262(1)	85.361(1)
γ (°)	75.980(17)	67.288(1)	81.907(1)
$V(Å^3)$	1978.3(7)	903.20(5)	2062.56(5)
Ζ	1	2	2
$\mu ({\rm mm}^{-1})$	1.05	1.258	1.218
Data collected	8050	12 462	18 679
Unique data	6951	4145	8927
R _{int}	0.0208	0.0356	0.0503
Final R_1	0.0545	0.0553	0.1207
Final $R_{\rm w}^2$	0.161	0.142	0.3328

Michael type reaction [23]. An excess of the 'activated' vinylaromatic was added to a THF solution of the free macrocycle to which an excess of "BuLi had been added. After removal of solvents, the residue was converted to the hydrochloride salt, extracted into water then basified to liberate the free amine. In the case of those reactions involving 2,4,6-trimethylstyrene, the single pendent arm product was the only one isolated. When the Michael acceptor was styrene or *p*-vinylanisole, the N', N'' disubstituted product was the only one isolated after work up. This variation is curious and no explanation is apparent. The ligands L_6-L_7 were prepared by the conventional mono-functionalization technique of reacting the appropriate arylalkyl halide with 1,4,7-triazacyclo[5.2.1.04.10]decane followed by base hydrolysis (Scheme 3).

3.2. Synthesis of the complexes

The complexes were prepared by addition of the free ligand to ethanolic or water solutions of the appropriate metal salts. The solid complexes could be obtained as precipitates by addition of a suitable counter ion $((PF_6)^- \text{ or } (ClO_4)^-)$. In the case of the neutral complex 1, the product was precipitated from ethanolic solution by the addition of diethyl ether. Crystals suitable for X-ray crystallography were obtained for complexes 1, 14 and 16.

3.3. Description of the crystal structures

The structure of the two different cations found in the unit cell of complex **1** are illustrated in Fig. 1. In the first case the Cu(II) metal ion is coordinated to the three nitrogens of the macrocycle with the two other sites occupied by chloride ions. The Cu–N bond lengths



Scheme 3. Reactions used in the preparation of *N*-funtionalized triazamacrocycles.



Fig. 1. ORTEP for Windows [30] plot of: (A) [Cu(L₁)Cl₂]; and (B) $[Cu(L_1)_2]^{2+}$ (thermal ellipsoids are shown at 50% probability and hexafluorophosphate anions are omitted or clarity); selected bond lengths (Å) and angles (°): Cu2-N21, 2.268(3); Cu2-N24, 2.045(4); Cu2-N27, 2.040(4); Cu2-Cl1, 2.295(1); Cu2-Cl2, 2.253(1); N27-Cu2-N24, 81.71(15); N27-Cu2-Cl2, 154.03(11); N24-Cu2-Cl2, 89.12(11); N27-Cu2-N21, 83.64(14); N24-Cu2-N21, 82.08(14); Cl2-Cu2-N21, 119.25(10); N27-Cu2-Cl1, 91.22(12); N24-Cu2-Cl1, 172.61(11); Cl2–Cu2–Cl1, 98.21(5); N21–Cu2–Cl1, 95.05(10); Cu1-N11, 2.571(4); Cu1-N14, 2.056(3); Cu1-N17, 2.023(4);180.00(18); N17-Cu1-N14, N17-Cu1-N17, 82.54(15); N17-Cu1-N14, 97.46(15); N17-Cu1-N14, 97.46(15); N17-Cu1-N14, 82.54(15); N14-Cu1-N14, 180.0(2).



Fig. 2. ORTEP for Windows [30] plot of $[Cu(L_6)(NO_3)_2]$ (thermal ellipsoids are shown at 50% probability); selected bond lengths (Å) and angles (°): Cu–N1, 2.243(3); Cu–N4, 2.005(3); Cu–N7, 2.016(3); Cu–O100, 1.952(3); Cu–O200, 2.018(3); O100–Cu1–N4, 177.77(13); O100–Cu1–N7, 97.27(13); N4–Cu1–N7, 84.65(13); O100–Cu1–O200, 85.63(13); N4–Cu1–O200, 92.47(13); N7–Cu1–O200, 176.90(12); O100–Cu1–N1, 94.16(12); N4–Cu1–N1, 84.88(12); N7–Cu1–N1, 84.46(11); O200–Cu1–N1, 96.47(10).

are consistent with a complex that is Jahn-Teller distorted, affording the cation a square-based pyramidal geometry. The pendant mesitylene is non-coordinated which is compatible with the 'soft' nature of the ligand. The second cation is a six coordinate centrosymmetric copper complex containing two macrocycles. Again the complex is Jahn-Teller distorted with two long bonds, the Cu-N (axial) bond length significantly greater than that found in the five coordinate complex. The pendant mesitylene group is well separated from the copper centre suggesting that steric hindrance is not a major factor in rationalising the lack of any reaction of the group with organometallic reagents (see later).

For complexes containing the ligands L_6 and L_7 , the alcohol and carboxyl groups, respectively are, in contrast to most pendant arm macrocyclic ligands, not available for binding to the same metal ion centre. For complexes of the two ligands intermolecular bonding is however feasible, and hence affords a way to create well-defined supramolecular structures. Illustrated in Fig. 2 is the structure of the complex $[Cu(L_6)(NO_3)_2]$, and collected is a list of selected bond lengths and angles. The complex is five-coordinate and, as observed for the previously discussed copper systems, has a Jahn-Teller distorted square-based pyramidal structure. The two nitrate ions act as monodentate ligands and the pendant aromatic group is well separated from the copper-tacn core. The oxygen of the benzylalcohol segment is disordered over two sites consistent with a lack of intermolecular bonding to an adjacent unit. Indeed, no weak forces such as H-bonding to the nitrate ions are evident in the crystal-packing diagram.

In contrast to the previous complex the structure of the Cu(II) system containing the ligand L_7 displays a more interesting recognition phenomenon as depicted in Fig. 3. As before the three nitrogens of the macrocycle are all coordinated and the pendant aromatic is well separated from the Jahn-Teller distorted Cu(II) centre. Unlike the copper complex of L_6 the carboxyl oxygen from a neighbouring unit coordinates to the copper so that the asymmetric unit contains a basic $[Cu_2(L_7-H)_2]^{2+}$ repeat unit. As a result, a one-dimensional coordination polymer is produced as illustrated in the packing diagram of Fig. 4. A water molecule completes the fifth coordination sphere of each copper and it is noted that these water molecules point in the same direction but do not hydrogen bond to the layer above. The 'L' motif of the complex has dimensions of approximately 9.5×11 Å², which leads to speculation that further self-assembly using an appropriate template could generate a tetracopper molecular box (Scheme 2). Such control of molecular self-assembly is currently of great interest but as of yet has not utilised triazamacrocycles containing pendant arms. Further coordination studies of ligands based on L₇ are underway and will be reported at a later date.



Fig. 3. ORTEP for Windows [30] plot of $[Cu_2(L_7-H)_2(H_2O)_2]^{2+}$ (thermal ellipsoids are shown at 50% probability and hexafluorophosphate anions and extraneous water molecules are omitted or clarity); selected bond lengths (Å) and angles (°): Cu1-N11, 2.235(6); Cu1-N14, 2.021(7); Cu1-N17, 2.035(7); Cu1-O1, 1.981(6); Cu1-O21, 1.946(6); Cu2-N21, 2.246(7); Cu2-N24, 2.024(8); Cu2-N27, 2.035(9); Cu2-O2, 1.978(7); Cu2-O11, 1.932(6); O21-Cu1-O1, 92.4(3); O21-Cu1-N14, 175.3(3); 01-Cu1-N14, 91.6(3); O21-Cu1-N17, 90.2(3); O1-Cu1-N17, 168.1(3); N14-Cu1-N17, 85.4(3); O21-Cu1-N11, 97.6(2); 01-Cu1-N11, 107.4(2); N14-Cu1-N11, 83.4(3); N17-Cu1-N11, 83.7(3); O11-Cu2-O2, 93.2(3); O11-Cu2-N24, 175.0(4); O2–Cu2–N24, 91.5(4); O11-Cu2-N27, 89.0(4); O2-Cu2-N27, 166.6(3); N24-Cu2-N27, 86.0(4); O11-Cu2-N21, O2-Cu2-N21, 109.6(3); 96.0(3); N24-Cu2-N21. 83.9(3); N27-Cu2-N21, 83.2(3).

3.4. Description of the metal complexes

3.4.1. L_1 complexes

The L_1 complexes are all typical octahedral *bis* ligand species as expected for the metal ions concerned. As is described above, a second form of 1 is observed in the crystal, namely a neutral 1:1 dichloro-complex. This five coordinate species is analogous to the copper complex of *N*-(5-pent-2-yne)-1,4,7-triazacyclononane described elsewhere [11]. Solutions of the pale pink cobalt complex rapidly darken in air suggesting oxidation to Co(III), though no single species could be obtained from the dark solutions.

The 'hard' Lewis acidic metal centres in these complexes do not interact with the pendent arm arene groups, and coordination takes place exclusively through the ring nitrogens. For example, the ¹³C NMR of the zinc complex **3** shows the signals due to the arene



Fig. 5. Proposed folding of the cyclen macrocycle to generate a *cis*-complex.

moiety to be essentially unshifted from those of the free ligand.

3.4.2. L_4 complexes

The copper complex 5 is, as isolated in the solid state, a 1:1 species containing a four coordinate Cu(II) centre [24], though it may well become five coordinate in solution. When L_2 in butan-1-ol is added to Ni(ClO₄)₂·6H₂O in hot butan-1-ol, a green solid precipitates from solution. This species shows three visible bands in nitromethane solution at 882, 586 and 443 nm, respectively. On this basis, we postulate a five- or six-coordinate nickel species. The size of the macrocyclic cavity in the 12 membered cyclen ring is such that square coplanar coordination of the metal is unlikely. The ligand rather is wrapped around the metal forming a *cis* complex [25], with the remaining coordination sites occupied by water (Fig. 5).

The blue liquor from the reaction yields, on removal of the solvent, a yellow solid. This dissolves in nitromethane or acetonitrile to give blue solutions. The yellow colour of the solid suggests a four-coordinate square coplanar environment for the nickel atom. This behaviour is well documented and Lincoln and coworkers [24] have described such a high spin-low spin equilibrium for the nickel complex of 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (tmc) (Eq. (1)).

1,4,7,10-tetraazacyclododecane (tmc) (equation 1).

$$[Ni(tmc)]^{2^+} + H_2O \iff [Ni(tmc)H_2O]^{2^+} \quad (1)$$

low spin

high spin

In addition, Fabbrizzi [26] has noted that in aqueous solutions of the nickel complex of cyclen, the normal blue colour of the octahedral high spin species becomes yellow on addition of 6 M $LiClO_4$ when heated, and the electronic spectrum, showing a new band at 23 000



Fig. 4. ORTEP for Windows [30] view down the *a*-axis of the coordination polymer generated by the repeating $[Cu_2(L_7-H)_2(H_2O)_2]^{2+}$ moiety.

 cm^{-1} becomes more typical of a low spin square planar species. Unfortunately, electronic spectra of the yellow form of 7 were not available in solution, as any solvent which led to dissolution, regenerated the octahedral form.

3.4.3. L_5 complexes

The macrocyclic cavity of the larger 14-membered ring is large enough to accommodate the metal ions Cu(II) and Ni(II) in square coplanar coordination. The UV–Vis spectrum of $[Ni(L_5)](ClO_4)_2$ (9) in methanol $(\lambda = 463 \text{ nm}, \varepsilon_{max} = 79 \text{ mol}^{-1} 1 \text{ cm}^{-1})$ is consistent with a four coordinate complex. On addition of an excess of LiCl, a mauve solid separates from an acetone solution, which may be identified as $[Ni(L_5)Cl_2]$ (10). This complex may also be prepared by addition of free ligand to NiCl₂·6H₂O in ethanol [27]. The UV–Vis spectrum of 10 in methanol is identical to that of 9 indicating the ionisation of the two chlorides in methanolic solution.

3.4.4. L_6 complexes

The complexation of L_6 with Ni(II) produced a pale pink solid which exhibited three bands in the UV–Vis region at 885, 533 nm and a shoulder at 316 nm, respectively. The mass spectrum of the complex revealed a prominent ion at m/z = 701 which is assigned to the [Ni(L_6)₂](PF₆)⁺ ion. Interestingly a weaker peak as also observed in the mass spectrum at m/z = 1547which can be attributed to a dimeric [Ni(L_6)₂]₂(PF₆)₃⁺ ion. It is possible that weak intermolecular H-bonds between the hydroxyl groups are responsible for the self-aggregation (Fig. 6).

The cobalt complex of L_6 is dark claret in colour and displays one band at 539 nm in the UV–Vis region. The mass spectrum of the complex reveals a prominent ion at m/z = 370 which is compatible with the $[Co(L_6)NO_3]^+$ ion. The IR and elemental analysis supports the existence of coordinated water so that as in the nickel case the complex is six-coordinate. Unlike the cobalt complex of L_1 a solution of 13 exhibits no observable change in air suggesting that oxidation to Co(III) is slow.

3.5. Attempts to coordinate the pendent arene arm

Electron rich arenes such as mesitylene (1,3,5trimethylbenzene) are excellent π acceptor ligands to-



Fig. 6. Proposed dimerization of $[{\rm Ni}(L_6)_2]^{2\,+}$ by H-bonding of the alcohol groups.

wards 'softer' transition metals. Such metal species as $[Rh(COD)]^+$, generated in situ from $[Rh(\mu-Cl)(COD)]_2$ (COD = 1,5-cyclooctadiene) and AgPF₆ react smoothly with arenes at room temperature to give η^6 arene complexes [28,29]. However, in our hands, reaction of either L₁ or the zinc complex **3** with $[Rh(COD)](PF_6)$ in refluxing THF showed no reaction of the arene ring after 24 h. In the former case, ¹H NMR spectroscopy indicated reaction of the rhodium centre with the macrocycle ring nitrogens, but addition of further $[Rh(COD)](PF_6)$ did not lead to the formation of an η^6 complex. Clearly, the presence of the ring nitrogens must have a considerable deactivating effect on the arene moiety.

4. Conclusions

A number of aromatic functionalized azamacrocycles have been prepared along with their metal complexes. Electron rich aromatics can be selectively incorporated into tri- and tetra-azamacrocycles in good yields using Michael-type chemistry. Complexation via the macrocycle nitrogens to hard metal ions is facile but unfortunately the π -rich aromatics do not react with soft metal ions to create mixed metal systems.

The Cu(II) complex of a single pendant arm benzylcarboxylic acid funtionalized 1,4,7-triazacyclononane macrocycle displays interesting self-assembly properties. This recognition phenomenon has the potential to be exploited in the creation of large superstructures with interesting magneto properties, and hence the generation of novel inorganic materials.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 166329 ,166330, 166331 for compounds **1**, **14** and **16**. Copies of the data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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