Polyhedron 30 (2011) 1530–1537

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

The use of hydrogenated Schiff base ligands in the synthesis of multi-metallic compounds II ☆

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A R T I C L E I N F O

Article history:
Received 25 January 2011
Accepted 3 March 2011
Available online 21 March 2011

Keywords:
Multidentate
Schiff base
Nickel
Copper
Zinc controlled organisation

A B S T R A C T

Tris(2-hydroxybenzylaminoethyl)amine (H_3L) complexes of nickel, copper and zinc are investigated as potential metallo-ligands ([(H_xL)M]; $x = 0, 1$: M = Ni, Cu, Zn). The homometallic complexes formed are dimetallic ([{(HL)Ni}Ni$(OAc)_2$] and [{(L)Zn}ZnCl]), tetrametallic ([{(L)Cu}Cu]$_2^{2+}$) and hexametallic ([{(L)Ni}Ni_2(μ-OH)$_2$(OEt)(OH_2)]$_2$). Hetero-dimetallic complexes can be formed with [(HL)Ni] and copper chloride ([{(HL)Ni}$CuCl_2$]) or zinc bromide ([{(HL)Ni}$ZnBr_2$]). The metallo-ligand acts as a chelating agent using phenolate pairs. The remaining phenolate either does not coordinate or can be used to increase the number of metals included in the scaffold from two to four or six. Not all combinations are possible and [(HL)Cu]$^+$ produces a charge separated species with zinc chloride rather than a complex. An exchange reaction is observed to take place when [(HL)Zn]$^+$ is treated with the halides of nickel or copper producing [(HL)M]$^+$ (M = Ni, Cu, respectively).

1. Introduction

Multidentate ligands such as tris(2-hydroxybenzylaminoethyl)amine (H_3L) and related systems have been of some interest over the past 10 years as they offered a direct route to the synthesis of mixed trimetallic d–f metal complexes (Fig. 1) for magnetochemical studies [1–5]. The synthesis of species such as [{(L)Ni}$_2$Ln(HOMe)]$^+$ (Ln = lanthanoid) were typically achieved by the direct reaction of the ligand (H_3L) with the nitrate salts of nickel and the desired lanthanoid. The complexes self-assemble in solution with the transition metal choosing to bind preferentially to the four nitrogen donors and the lanthanoid exclusively to the phenolates. These complexes do not have C_3 symmetry as only two of the phenolates are used to bridge the metals. The absence of information on the simple complexes of H_3L with nickel, which must form during the synthesis of these species, led us to the isolation of the intermediate complex [(H_xL)Ni]$^+$ ($x = 1, 2$) including the related copper and zinc complexes [(H_2L)M]$^+$ (M = Cu, Zn) [6]. Although the three transition metal complexes have identical empirical formula they are not isostructural (Fig. 1). The nickel sits in a six coordinate N_4O_2 environment whereas the copper and zinc complexes are five coordinate employing an N_4O coordination sphere. As a consequence of the protonated phenolate (Fig. 1c) the nickel complex remains cationic.

The subtle differences in the structures of the nickel and copper complexes (Fig. 1) go some way to explain why the synthesis of the analogous mixed copper–lanthanoid complexes of H_3L cannot be isolated [6]. Instead of forming a trimetallic $LnCu_2$ complex with H_3L we obtain the trimetallic copper complex [$(HL)_2Cu_3$]$^{4+}$ (Fig. 2). Extending our studies to include alkali metals we recently reported that nickel again had a preference for tetrametallic (Ni_2K_2) complexes such as [{(L)Ni}Kμ-(EtOH)]$_2$ whereas copper and zinc generated larger multimetallic complexes such as [({(L)Cu}K)(OH_2)$_4$-μ$_4$-OH_2] (Fig. 2), which contain a K_4O core and are essentially 1:1 K:Cu and K:Zn, respectively [7].

We are beginning to regard complexes such as [(H_xL)M]$^+$ as potential ligands [7]. Complexes such as [{(L)Ni}$_2$Ln(HOMe)]$^+$ demonstrate that, with the correct conditions, it is possible to overcome the positive charge on the primary complex and organise the phenolate donors such that they create a binding site for metals [4–7]. Thus far the greatest success has been had with divalent metals, such as nickel, which prefers an octahedral geometry and which leave a residual negative charge on the metallo-ligand. However, our recent work [7] on the alkali metal adducts of [(HL)M]$^+$ suggested that this concept could be extended to the corresponding metal complexes of copper and zinc as long as the charge on the metal centre being introduced is not too high ($\geqslant 3$). To investigate this hypothesis we have extended our studies on the H_3L adducts of nickel copper and zinc and their subsequent combination with the divalent transition metals nickel copper and zinc.

Abbreviations: HBTC, tris(hydroxybenzyl)triazacyclononane; HAME, tris (hydroxybenzyl)aminomethylethane; HAC, tris(hydroxybenzyl)aminocyclohexane; Salpr, bis(salicylidene)-1,3-propanediamine; TrenSal, tris(2-hydroxybenzylidene) aminoethylamine; H_3L, tris(2-hydroxybenzyl)aminoethylamine.

☆ For part I see Ref. [6].

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doi:10.1016/j.poly.2011.03.004

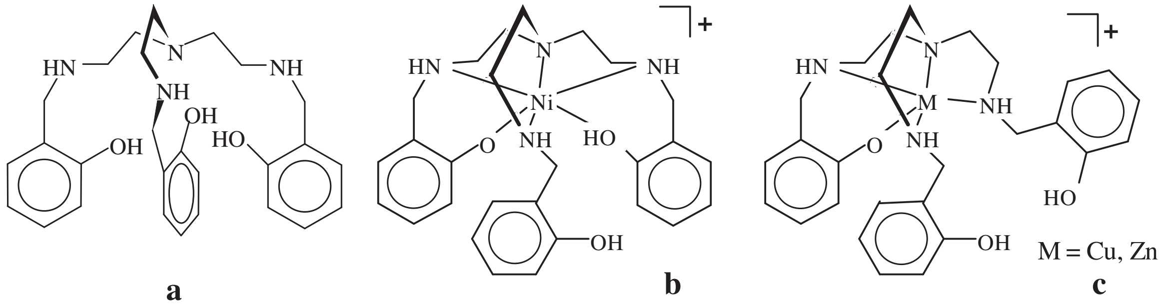

Fig. 1. Tris(2-hydroxybenzylaminoethyl)amine (H_3L) (a) and a schematic representations of its cationic nickel (b), copper and zinc (**c**) complexes; $[(H_2L)M]^+$ (M = Ni, Cu, Zn).

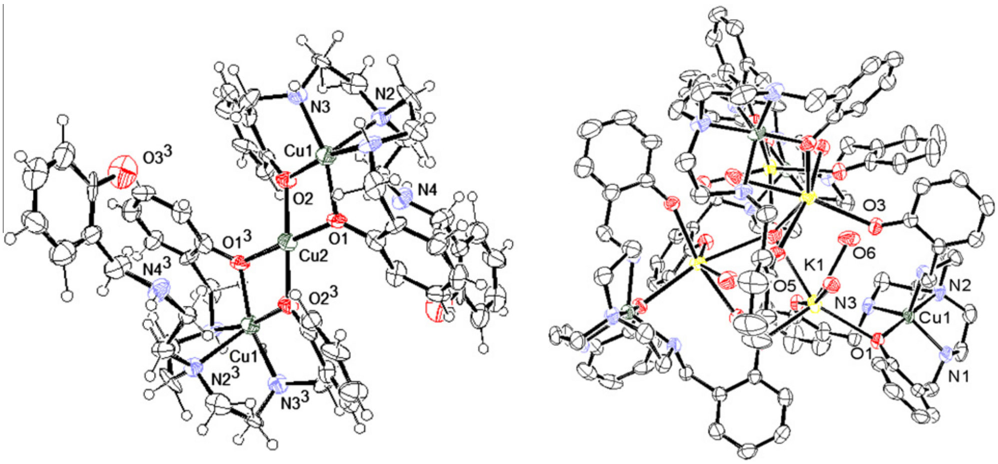

Fig. 2. (Left) The X-ray crystal structure of $[(HL)_2Cu_3]$ $4NO_3$. (Right) The X-ray crystal structure of $[(\{(L)Cu\}K)(OH_2)_4\text{-}\mu_4\text{-}OH_2]$. The expansion in the motif from trimetallic to octametallic is supported by the bridging nature of the pendant phenolates (cf nickel Fig. 1). These structures suggest that $[(H_2L)Cu]^+$ is capable of chelating low valent metals.

2. Experimental

All experiments were carried out using standard apparatus and commercially available chemicals. Tris(2-hydroxybenzylideneaminoethyl)amine (TrenSal) and tris(2-hydroxy-benzylaminoethyl)-amine (H_3L) were prepared as previously reported [6,8]. Solid reflectance spectra (400–900 nm) were recorded on a Photonics CCD array UV–Vis spectrophotometer. Mass spectra were recorded using a Thermo Finnigan LCQDuo by electrospray ion trap. Infra red spectra were recorded as potassium bromide discs using a Nicolet Avatar 360 FTIR spectrometer.

X-ray measurements were conducted using Oxford Diffraction and Nonius Kappa CCD diffractometers using graphite monochromated Mo Kα radiation, apart from $[\{(L)Zn\}ZnCl]$ and $[\{(HL)Ni\}CuCl_2]$ which were collected at Daresbury Synchrotron Radiation Source on a Bruker Smart APEX2 CCD diffractometer. Crystals were coated in mineral oil and mounted on glass fibres. Full matrix least-squares refinement to convergence was based on F^2. The structure solution and refinement used the programs SHELXS and SHELXL-97 [9] and the graphical interface WinGX [10]. A summary of the crystallographic and refinement parameters is given in Table 1. Full details are available in cif format as Supplementary Information.

2.1. Preparation of $[\{(HL)Ni\}Ni(OAc)_2]$

H_3L (1.10 g, 2.36 mmol) was dissolved in methanol (50 ml), followed by the addition of nickel (II) acetate tetrahydrate (1.17 g, 4.72 mmol). The mixture was brought to reflux for 60 min, the resultant bluish solution was allowed to cool and then filtered. The methanol was removed and the product recrystallised from acetonitrile/diethyl-ether by vapour diffusion. Yield 67%. *Anal.* Calc. for $C_{31}H_{40}N_4Ni_2O_7$: C, 53.33; H, 5.78; N, 8.03. Found: C, 53.19; H, 6.10; N, 8.22%. FTIR [(ν/cm^{-1} (KBr)]: 3430, 2995, 1565, 1480, 1275, 770. Mass spec. (ESI) *m/z* 521 (LNi^+). λ_{max} (solid reflectance) no bands.

2.2. Preparation of $[\{(L)Ni\}Ni_2(\mu\text{-}OH)_2(\mu\text{-}OEt)(OH_2)]_2$ NO_3 Cl

H_3L (0.1 g, 0.22 mmol) was dissolved in ethanol (20 ml), followed by addition of $Ni(NO_3)_2{\cdot}6H_2O$ (0.06 g, 0.22 mmol). The mixture was stirred at 50 °C after which three drops of triethylamine was added. $NiCl_2{\cdot}6H_2O$ (0.07 g, 0.30 mmol) was added. The greenish solution was refluxed for 1 h, allowed to cool and filtered. Crystals were grown directly from the mother liquors by vapour diffusion with diethyl-ether. Yield 32%. *Anal.* Calc. for $C_{58}H_{84}N_9Cl_1O_{17}Ni_6{\cdot}5H_2O$: C, 42.04; H, 6.81; N, 7.61. Found: C, 41.76; H, 7.05; N, 7.62%. FTIR [(ν/cm^{-1} (KBr)]: 3450, 2925, 1635, 1600, 1480, 1383, 1285, 760. Mass spec. (ESI) *m/z* 521 (100% LNi^+), 1063 (10% L_2Ni_2Na), 1099 (1% L_2Ni_3). λ_{max} (solid reflectance) 560, 630, 950.

2.3. Preparation of $[\{(L)Cu\}Cu]_2$ $[NO_3]_2$

H_3L (0.92 g, 2.0 mmol) was dissolved in methanol (15 ml), followed by the addition of copper nitrate (0.75 g, 4.0 mmol) in methanol (10 ml). The mixture turned dark green. After stirring for 10 min a few drops of triethylamine were added upon which the solution became cloudy. The solution was filtered to give a green powder. X-ray quality crystals were grown from the slow

Table 1
Selected crystallographic and refinement parameters.

	$[\{(HL)Ni\}Ni(OAc)_2]$	$[\{(L)Ni\}Ni_2(\mu\text{-}OH)_2(OEt)\text{-}(OH_2)]_2\ [Cl_{1.33}\ (NO_3)_{0.67}]\cdot xH_2O$	$[\{(L)Cu\}Cu]_2\ 2NO_3\cdot 3MeOH$	$[\{(L)Zn\}ZnCl]\cdot MeOH$	$[\{(HL)Ni\}CuCl_2]\ MeNO_2$	$[\{(HL)Ni\}\ ZnBr_2]\cdot MeOH$	$[(H_2L)Cu]^+\ Et_3NH^+\ [ZnCl_4]^{2-}$
Empirical formula	$C_{31}H_{40}N_4Ni_2O_7$	$C_{59.6}H_{86}Cl_{1.34}N_{8.66}Ni_6O_{16.77}$[A]	$C_{57}H_{78}Cu_4N_{10}O_{15}$	$C_{28}H_{37}ClN_4O_4Zn_2$	$C_{28}H_{37}Cl_2CuN_5NiO_5$	$C_{28}H_{37}Br_2N_4NiO_4Zn$	$C_{33}H_{51}Cl_4CuN_5O_3Zn$
Formula weight	698.09	1591.89	1397.45	659.81	716.78	777.52	836.50
Crystal system	$P2_1/n$	$P\bar{1}$	$P2_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Space group	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
a (Å)	13.2085(3)	11.1482(5)	12.6994(5)	18.744(3)	8.9235(9)	11.5412(4)	10.9046(4)
b (Å)	17.7615(3)	11.5773(3)	17.2400(7)	8.8981(12)	22.086(2)	15.2088(5)	12.9133(4)
c (Å)	13.7552(3)	15.9213(7)	14.8768(5)	17.531(2)	15.3655(15)	17.8402(6)	14.9948(4)
α (°)		103.717(3)				94.130(3)	81.563(2)
β (°)	98.173(2)	91.233(3)	108.853(2)	92.1470(10)	90.841(2)	98.336(3)	69.780(2)
γ (°)		114.348(3)				94.964(3)	71.069(2)
Z	4	1	2	4	4	4	2
V (Å^3)	3194.23(11)	1802.14(12)	3082.3(2)	2921.9(7)	3027.0(5)	3075.37(18)	1872.76(10)
T (K)	123	123	123	120	120	123	120
λ (Å)	0.71073	0.71073	0.71073	0.67100	0.67100	0.71073	0.71073
μ_{calc} (mm^{-1})	1.231	1.653	1.434	1.773	1.547	2.194	1.533
No. of reflections measured	34 059	33 023	29 534	27 063	22 905	27 496	41 215
No. of unique reflections	7698	7051	13 472	8701	5351	12 065	8581
R_{int}	0.0324	0.0431	0.080	0.0604	0.0782	0.0683	0.0626
No observed	6023	5348	9998	7329	3922	5564	6320
No. of parameters	400	431	782	354	385	685	451
R^a ($I > 2\sigma(I)$)	0.0299	0.0575	0.0538	0.0467	0.0484	0.0417	0.0425
$R_w{}^b$ (all reflections)	0.0791	0.1483	0.0912	0.1367	0.1288	0.0774	0.0848
Goodness-of-fit (GOF)	0.978	1.032	1.039	0.990	1.027	0.732	1.015
Instrument	Nonius Kappa	Oxford Gemini S	Nonius Kappa	Daresbury SRS	Daresbury SRS	Oxford Gemini S	Nonius Kappa

[A] Indicates that the program SQUEEZE was used to remove small amounts of disordered solvent from the model crystal structure. This has not been included in the given formula but is calculated to be roughly equivalent to five water molecules.

evaporation of the mother liquor. Yield 67%. *Anal.* Calc. for $C_{54}H_{66}N_{10}O_{12}Cu_4$ 2MeOH: C, 49.26; H, 5.46; N, 10.26. Found: C, 49.21; H, 5.32; N, 10.54%. FTIR [(ν/cm^{-1} (KBr)]: 2925, 1634, 1562, 1408, 1383, 1276, 1020, 871, 753. Mass spec. (ESI) *m/z* 526 (100%, LCu$^+$). λ_{max} (solid reflectance) 670 nm.

2.4. Preparation of [{(L)Zn}ZnCl]

H_3L (0.1 g, 0.22 mmol) was dissolved in methanol (15 ml), to which was added $Zn(NO_3)_2{\cdot}6H_2O$ (0.06 g, 0.22 mmol). The mixture was stirred at 50 °C for 5 min, followed by addition of two drops of triethylamine. A methanolic (5 ml) solution of $ZnCl_2$ (0.03 g, 0.22 mmol) was added to the mixture drop-wise to obtain a brownish solution. This was allowed to cool and filtered. Crystals were grown by the slow evaporation of the mother liquor. Yield 47%. *Anal.* Calc. for $C_{27}H_{33}N_4O_3Zn_2Cl{\cdot}MeOH{\cdot}3H_2O$: C, 47.11; H, 6.07; N, 7.85. Found: C, 47.25; H, 5.15; N, 8.12%. FTIR [(ν/cm^{-1} (KBr)]: 3426, 2934, 1485, 1275, 763. Mass spec. (ESI) *m/z* 527 (100%, LZn$^+$), 593 (20%, LZn$_2$$^+$).

2.5. Preparation of [{(HL)Ni}CuCl$_2$]

H_3L (0.1 g, 0.22 mmol) was dissolved in methanol (15 ml), to which was added $Ni(NO_3)_2{\cdot}6H_2O$ (0.06 g, 0.22 mmol). The mixture was stirred at 50 °C for 5 min, followed by the addition of two drops triethylamine. A methanolic solution (5 ml) of $CuBr_2$ (0.05 g, 0.22 mmol) was added dropwise to the mixture. The solution changed colour immediately from purple to brown. The solution was allowed to cool and filtered to produce a brown powder which was recrystallised from nitromethane. Yield 68%. *Anal.* Calc. for $C_{27}H_{34}N_4Cl_2Cu_1O_3Ni_1{\cdot}MeNO_2$: C, 46.92; H, 5.20; N, 9.77. Found: C, 46.44; H, 5.05; N, 9.17%. FTIR [(ν/cm^{-1} (KBr)]: 2925, 1610, 1480, 1390, 760. Mass spec. (ESI) *m/z* 521 (100%, LNi$^+$). The parent ion (*m/z* 526) of $[(H_2L)Cu]^+$ is a prominent feature of the mass spectrum of the reaction solution indicative of some metal exchange. λ_{max} (solid reflectance) 480, 820.

2.6. Preparation of [{(HL)Ni}ZnBr$_2$]

H_3L (0.1 g, 0.22 mmol) was dissolved in methanol (15 ml), to which was added $Ni(NO_3)_2{\cdot}6H_2O$ (0.06 g, 0.22 mmol). The mixture was stirred at 50 °C for 5 min, followed by the addition of two drops of triethylamine, after which methanolic (5 ml) solution of $ZnBr_2$ (0.05 g, 0.22 mmol) was added drop-wise. The light purple mixture was stirred for further 10 min, allowed to cool and filtered. Crystals were obtained by slow evaporation of the saturated solution. Yield 72%. *Anal.* Calc. for $C_{27}H_{33}N_4O_3Ni_1Zn_1Br_2{\cdot}MeOH$: C, 43.20; H, 4.80; N, 7.04. Found: C, 42.90; H, 5.01; N, 7.04%. FTIR [(ν/cm^{-1} (KBr)]: 3406, 2980, 1475, 1255, 758. Mass spec. (ESI) *m/z* 521 (100%, LNi$^+$). λ_{max} (solid reflectance) 555, 950.

2.7. Preparation of [(H$_2$L)Cu] Et$_3$NH$^+$ [ZnCl$_4$]

H_3L (0.23 g, 0.5 mmol) was dissolved in methanol (15 ml), followed by addition of $Cu(NO_3)_2{\cdot}2.5H_2O$ forming a green solution of $[(H_2L)Cu]^+$. The solution was stirred at 50 °C for 5 min. Four drops of triethylamine was added and the mixture stirred for a further 2 min. A methanolic (5 ml) solution of $ZnCl_2$ (0.07 g, 0.05 mmol) was added drop-wise and the pale green mixture allowed to cool. The solution was filtered and allowed to stand. X-ray quality crystals were grown by slow evaporation of the saturated solution. Yield 82%. *Anal.* Calc. for $C_{33}H_{51}Cl_4Cu_1N_5O_3Zn_1$: C, 42.78; H, 6.64; N, 7.56. Found: C, 42.77; H, 5.19; N, 7.69%. FTIR [(ν/cm^{-1} (KBr)]: 2980, 1603, 1480, 1265, 765. Mass spec. (ESI) *m/z* 526 (100%, LCu$^+$).

2.7.1. Reactions of [(H$_2$L)Cu]$^+$ with nickel halides

This reaction was carried as described above on a 0.5 mmol scale. The products obtained from the reaction was consistent with $[(H_2L)Cu]^+$ [7]. The parent ion (*m/z* 521) of $[(H_2L)Ni]^+$ is a dominant feature of the mass spectrum of the reaction solution indicative of some metal exchange.

2.7.2. Reactions of [(H$_2$L)Zn]$^+$ with nickel or copper halides

These reactions were carried as described above on a 0.5 mmol scale. The products obtained were consistent with $[(H_2L)Ni]^+$ and $[H_2L)Cu]^+$, respectively [7].

2.8. Preparation of [(HL)Fe]NO$_3$

H_3L (0.13 g, 0.28 mmol) was dissolved in methanol (30 ml) followed by addition of $Fe(NO_3)_3{\cdot}9H_2O$ (0.11 g, 0.28 mmol). To the brown mixture three drops of KOH solution (in methanol) was added, the mixture was refluxed for 1 h, allowed to cool and filtered. Crystals were grown directly from the mother liquors by vapour diffusion with diethyl-ether. Although the crystals were subjected to crystallographic analysis the data obtained failed to refine to a satisfactory solution (see Supplementary material). Crystal data: [(HL)Fe], orthorhombic *Pc*21*a*, a = 21.7392(18) Å, b = 7.2251(4) Å, c = 38.0527(31) Å, V = 5979.61(8) Å^3. *Anal.* Calc. for $C_{27}H_{34}N_5O_6Fe$: C, 56.01; H, 5.90; N, 11.61. Found: C, 56.01; H, 5.90; N, 12.06%. FTIR [(ν/cm^{-1} (KBr)]: 1475, 1265, 1388,, 615. Mass spec. (ESI) *m/z* 518 (100%, LFe$^+$); 1090 (29%, KL$_2$Fe$_3$$^+$). λ_{max} (solid reflectance) 475 nm.

3. Results and discussion

The multidentate ligand systems H_3L can be prepared with ease by hydrogenating the Schiff base species generated from the tris (2-aminoethyl)amine and salicylaldehyde [8]. Treatment of H_3L *in situ* with three equivalents of nickel acetate produced an off-white material. It is notable that the parent $[(H_2L)Ni]^+$ has a prominent band in the near infra-red (950 nm) which is absent in this product. Recrystallisation revealed the complex to be dimetallic; namely [{(HL)Ni}Ni(OAc)$_2$] (Fig. 3). The internalised nickel is coordinated by an N_4O_2 motif in a similar manner to $[(H_2L)Ni]^+$ [6]. However, the additional pendant phenoxide is not deprotonated and consequently the metallo-ligand does not carry a negative charge. Nickel acetate chelates to the phenolates (O1, O2) which

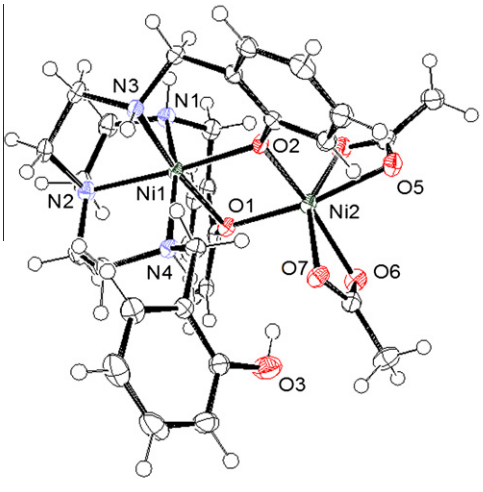

Fig. 3. The X-ray crystal structure of [{(HL)Ni}Ni(OAc)$_2$]. The metrical parameters of the [(H$_2$L)Ni] moiety are given in Table 2. The thermal ellipsoids are drawn at 50% probability.

are held close to one another by the encapsulated nickel. Heteroatomic nickel species such as $[\{(Salpr)Ni\}M(acac)_2]$ (M = Mn, Cu) which are loosely related to this complex have been reported previously by O'Conner et al. Central to this report is the manner in which the two phenolates of their tetradentate Schiff base ligand (Salpr) act as a didentate ligand to the diketonate of manganese and copper [11]. This motif would seem to be maintained here (Fig. 3) despite the presence of the third potential donor (*vide infra*). In the absence of any additional stabilising interaction from the pendant phenolate the dimetallic assembly is somewhat fragile and its mass spectrum is dominated by $[(H_2L)Ni]^+$ (*m/z* 521). Indeed its synthesis is best achieved in the presence of excess nickel acetate (Eq. (1) and (2)).

$$2Ni(OAc)_2 + H_3L \rightarrow [(H_2L)Ni]^+ + Ni(OAc)_2 \quad (1)$$

$$[(H_2L)Ni]^+ + Ni(OAc)_2 \rightleftarrows [\{(HL)Ni\}Ni(OAc)_2] \quad (2)$$

Employing nickel chloride instead of nickel acetate exchanges a didentate ligand for unidentate ligand which is also a good leaving group. These factors were expected to facilitate an increase in the metal content of the complex. With Schiff base ligands (e.g. TrenSal, Salpr) the product would be expected to be trimetallic [8,12]. However, with the more flexible H_3L the ligand accumulates three metal centres and dimerises to produce the hexametallic dicationic complex $[[\{(L)Ni\}Ni_2(\mu\text{-}OH)_2(OEt)(OH_2)]_2]^{2+}$ (Fig. 4). Using its phenolate donors (O1, O2), the [(L)Ni] ligand is again didentate to a second nickel (Ni2). One of the nickel amine (N4) interactions observed in $[\{(HL)Ni\}Ni(OAc)_2]$ (Fig. 3) is severed and its position occupied by a bridging hydroxide (O5). The amine phenolate released by Ni1 chelates to the third nickel (Ni3). The presence of a second bridging hydroxide (O6) completes the basic framework around which the Ni3 motif dimerises. An ethoxide and water complete the coordination sphere of the internal nickels (Ni2, Ni3). The nesting, open faced, cube motif at the centre of this structure is relatively common within nickel chemistry [13]. However, the presence of the additional nickel (Ni1) contained within [(L)Ni] as capping units lifts the complex into a more selective group of hexametallic nickel complexes [14–16]. Furthermore, the bond lengths and angles for the species retrieved are typical for this type of motif (Fig. 4, Table 2).

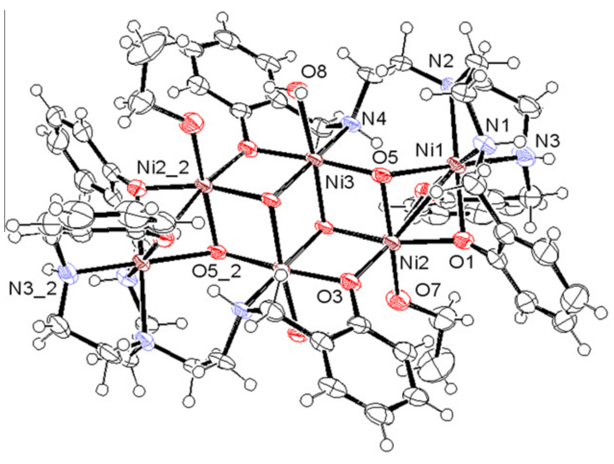

Fig. 4. The X-ray crystal structure of $[[\{(L\}Ni_2(\mu\text{-}OH)_2(OEt)(OH_2)]_2]^{2+}$. The disordered chloride and nitrate counter ions are not shown. The metrical parameters of the $[(H_2L)Ni]$ moiety are given in Table 2. Selected bond lengths and distances (Å) for the Ni_4O_8 core: Ni2–O3, 2.022(3); Ni1–O4, 2.103(3); Ni2–O2, 2.096(3); Ni3–O4, 2.051(3); Ni3–O5, 2.064(3); bond angles (°): O4–Ni2–O5, 83.4(1); O5–Ni3–O4, 82.9(1). The thermal ellipsoids are drawn at 50% probability.

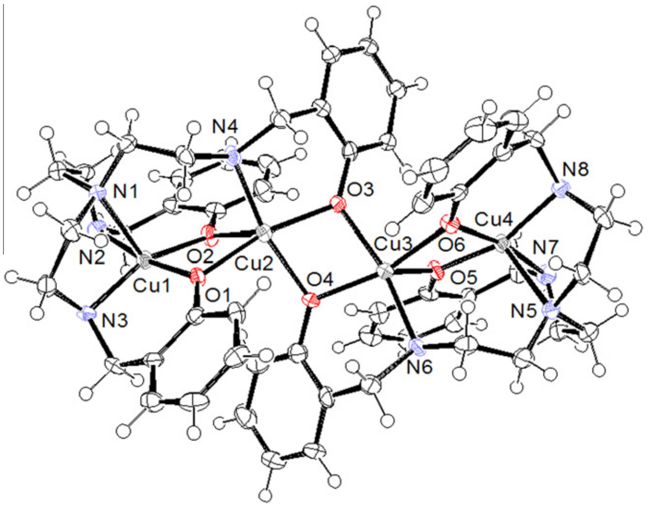

Fig. 5. The X-ray crystal structure of $[\{(L)Cu\}Cu]_2^{2+}$. The metrical parameters of the $[(H_2L)Cu]$ moiety are given in Table 2. Selected other bond lengths and distances (Å): Cu1···Cu2, 3.086; Cu2···Cu3, 3.056. Bond angles (°): Cu1–Cu2–Cu3, 146.27. The thermal ellipsoids are drawn at 50% probability.

Table 2
Selected geometric parameters for $[\{(HL)Ni\}Ni(OAc)_2]$, $[\{(L)Ni\}Ni_2(\mu\text{-}O)_2(OEt)(OH_2)]_2$ $[\{(L)Cu\}Cu]_2$ $2NO_3$, $[\{(L)Zn\}ZnCl]$, $[\{(HL)Ni\}CuCl_2]$, $[\{(L)Ni\}ZnBr_2]$ and $[\{(HL)Ni]^+$.

	M1–N2	M1–O1 M1–O2	M2–O1 M2–O2	M1···M2	N2–M1–N1	N2–M1–O1 N2–M1–O2	M1–O1–M2 M1–O2–M2	O1–M2–O2	N2–M1···M2
$[\{(HL)Ni\}CuCl_2]$	2.088(4)	2.099(3) 2.019(3)	1.969(3) 1.940(3)	3.1118(8)	82.68(15)	106.98(13) 177.23(13)	103.59(13) 99.76(13)	80.59(12)	145.45(10)
$[\{(HL)Ni\}ZnBr_2]$	2.108(4)	2.089(3) 2.101(3)	1.980(4) 1.974(3)	3.0482(9)	81.0(2)	105.70(15) 174.23(16)	96.99(14) 97.82(15)	84.64(14)	145.61(12)
$[\{(HL)Ni\}Ni(OAc)_2]$	2.114(2)	2.0795(12) 2.0454(12)	2.0421(12) 2.0114(11)	3.1211(3)	81.38(6)	106.11(5) 174.37(5)	98.44(5) 100.59(5)	81.22(5)	146.30(4)
$[[\{(L)Ni\}Ni_2(\mu\text{-}OH)_2(OEt)(OH_2)]_2]^{2+}$	2.141(4)	2.057(3) 2.032(4)	2.090(4) 2.096(3)	2.7463(8) 3.0675(8) (M2–M3)	85.63(16)	101.50(15) 177.27(16)	82.95(13) 83.39(13)	78.95(14)	132.83(11)
$[\{(L)Cu\}Cu]_2^{2+}$	2.338(4)	1.947(3) 1.922(3)	1.952(3) 2.225(3)	3.0861(8) 3.0556(8) (M2–M3)	82.60(16)	91.83(14) 116.61(15)	104.63(15) 95.90(14)	75.02(13)	
$[\{(L)Zn]\}ZnCl]$	2.2302(17)	2.1770(14) 2.0469(15)	1.9820(15) 1.9522(15)	3.0485(4)	80.28(6)	111.16(6) 169.23(6)	94.16(6) 99.31(6)	86.90(6)	151.55(4)
$[(HL)Ni]^+$ [6]	2.103	2.003 2.189			89.93	175.13 97.09			

The ability to generate multimetallic complexes of copper would seem to be more favourable as both Orvig and co-workers [5] and ourselves [6] have reported trimetallic species using members of this family of ligand (Fig. 2). Surprisingly, in this study the treatment of H_3L with copper nitrate generates the tetrametallic cation $[\{(L)Cu\}Cu]_2^{2+}$ (Fig. 5). Each of the copper centres sits in a five coordinate environment. Furthermore the terminal copper atoms (Cu1, Cu4) are in an unfamiliar N_3O_2 motif. Similar to $[[\{(L)Ni\}Ni_2(\mu\text{-}OH)_2(OEt)(OH_2)]_2]^{2+}$ and in contrast with $[(H_2L)Cu]^+$, one of the amine donors (N4) is displaced from the coordination sphere of the encapsulated metal in favour of a second phenolate (O2). The central copper atoms (Cu2, Cu3) sit in an NO_4 motif forming two chelates; one to the cleft of the L moiety (O1, O2) and a second with the pendant phenolate (O3) and its attendant secondary amine (N4). The complex achieves its tetrametallic nature through the bridging phenolates (O3, O4). The five coordinate nature of each of the copper centres help generate the gentle twist (<Cu–Cu–Cu–Cu, 122.6°) that passes through the core of the complex. A small number of tetrametallic complexes of copper have been reported. Of interest here is the complex, $([\{(Salpr)Cu]_2Cu(OAc)(OMe)]_2)$ reported by Fukuhara et al. [17]. This is constructed from the tetradentate copper Schiff base complex [(Salpr)Cu], complexed to a second copper, again through the phenolate donors and an acetate bridge (*pace* an internal phenolate O2, Fig. 5). The motif dimerises about a bridging methanol (*pace* the extended phenolate O3, Fig. 5). The copper atoms in $[\{(Salpr)Cu]_2Cu(OAc)(OMe)]_2$ have similar spacing (3.124 Å, 3.028 Å) and a similar undulation (<Cu–Cu–Cu, 147°) within the imaginary Cu4 chain to the complex reported here (Fig. 5). A major difference between copper and nickel is the propensity for nickel to utilise a greater number of donor atom positions than copper. For copper the remaining donors are not only sufficient in number but due to the flexibility of H_3L, they are placed forward of the second metal thus promoting dimerisation without the need for additional donors (e.g. hydroxide).

The zinc chemistry of TrenSal and H_3L demonstrates similarities to both nickel and copper. With TrenSal, zinc adopts the motif displayed by nickel namely an octahedral trimetallic complex [8], whereas with H_3L zinc follows copper [7] forming a five coordinate N_4O complex (Fig. 1). On treating H_3L with excess zinc chloride we obtained a second dimetallic complex (Fig. 6). The motif is a hybrid of that displayed by nickel (Figs. 3 and 4) and copper (Fig. 5). Similar to nickel the internalised zinc (Zn1) sits within an N_4O_2 motif. The bond distances and angles differ only by what might be expected when introducing a cation of slightly larger radius (Table 2). Similar to $[\{(HL)Ni\}Ni(OAc)_2]$, the external zinc chloride (Zn2) is again held between the chelating phenolates (O1, O2). However, in contrast to $[\{(HL)Ni\}Ni(OAc)_2]$ and similar to $[\{(L)Cu\}Cu]_2^{2+}$, the remaining phenolate coordinates. However, again it is projected beyond the second zinc filling one of the chloride coordination sites. Dimerisation to a tetrametallic complex in $[\{(L)Cu\}Cu]_2^{2+}$ is, we believe, driven by the reorganisation of the pendant phenolate which is used as a chelating site. In the zinc complex, the amine phenolate (N4) does not migrate from Zn1 to Zn2 and dimerisation does not occur. A number of simple dimetallic zinc complexes are known [18–19]. These comprise a zinc dihalide chelated to the two

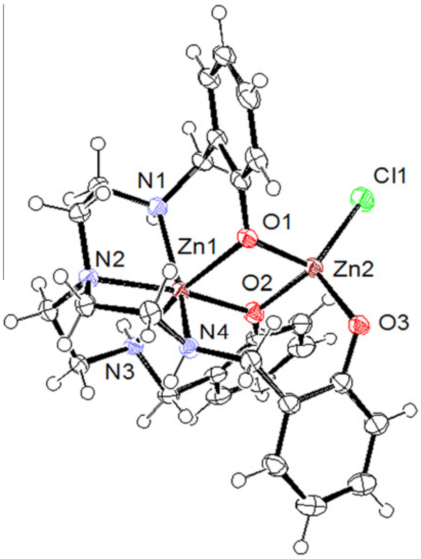

Fig. 6. The X-ray crystal structure of $[\{(L)Zn]\}ZnCl]$. The metrical parameters of the $[(H_2L)Zn]$ moiety are given in Table 2. The thermal ellipsoids are drawn at 50% probability.

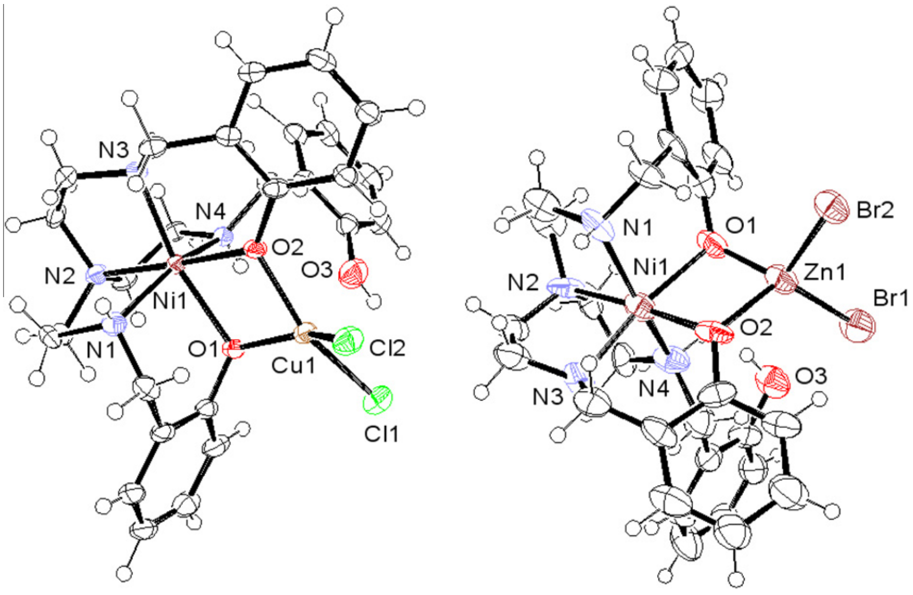

Fig. 7. The X-ray crystal structure of $[\{(HL)Ni]\}CuCl_2]$ and $[\{(HL)Ni]\}ZnBr_2]$. The metrical parameters can be found in Table 2. The thermal ellipsoids are drawn at 50% probability.

phenolates of a zinc Schiff base complex such as [(Salpr)Zn]. Displacement of a halide from these cannot occur as these tetradentate ligands lack the essential additional donor. The motif described here would seem to be somewhat rare [20] as reactions of Schiff base ligands in which additional donors (e.g. salicylidene, acetate) are present typically promote the formation of trimetallic complexes [8,21–24]. However, it is likely that this process is prevented here by the extended phenolate (O3) which encroaches on the space required by a second [$(H_2L)Zn$] unit.

The three homometallic species of nickel copper and zinc display widely different behaviour. Each with precedence in Schiff base chemistry [8]. The zinc species is probably the most easily understood as homometallic species where $ZnCl_2$ is complexed to the two phenolates are known. The species reported here is a subtle modification of this motif where the pendant phenolate (O3, Fig. 6) rotates into the coordination sphere of the metal displacing a halide. This species can be viewed as a precursor of the family of trimetallic (L_2M_3) complexes best exemplified by nickel. These trimetallic species readily form the more rigid hexa- and heptadentate Schiff base ligands [8] and with tetradentate ligands crucially with acetate bridges [11]. Thus when we revert to the use of halide precursors with nickel the motif can expand but in a more dramatic manner. Although it continues to dimerise it does so based on an Ni_3 unit rather than around a central nickel. The copper species [$\{(L)Cu\}Cu]_2^{2+}$ taken in conjunction with a similar copper complex, [$\{(HL)Cu\}_2Cu]^{4+}$ [5,6], is also instructive in this analysis. These two motifs show that the two [$(H_2L)Cu$] ligand can complex at single metal centre ([$\{(HL)Cu\}_2Cu]^{4+}$) or individually act as a ligand to a copper centre which then dimerises ([$\{(L)Cu\}Cu]_2^{2+}$). This latter pair of complexes confirm the importance of the synthetic design to the synthesis of these compounds.

It is interesting that none of the H_3L complexes isolated here make use of all three phenolate donors as a symmetric facially capping donor set. This contrasts with the behaviour of the other multimetallic tri-phenolate ligands, HBTC [5,25,26], HAME [27] and HAC [28], which do have this arrangement. However these are hexadentate and to encapsulate a metal cation in an octahedral environment all three phenolates are required. In an attempt to show that it is possible to bring the three phenolate donors into the coordination sphere of transition metals we prepared and isolated the ferric complex [(L)Fe]. The crystals which were obtained for this species refined poorly during crystallographic analysis. However, although it is impossible to extract any metrical parameters, the gross structural features could be identified which confirm that the iron coordinates to the three phenolates at the expense of a bond to one of the secondary amines. The motif is similar to that of [(L)Al] [29].

The ability to synthesize homometallic complexes is relatively straightforward as there can be no problem with site selection by the metals being used. A real test of the durability of species such as [$(H_xL)M$] as ligand system would be the ability to build heteronuclear species especially with other transition metals. Thus, treating H_3L sequentially with nickel nitrate and the halides of either copper and zinc respectively we were again able to retrieve complexes which could be fully characterised (Fig. 7) and which support our view that we are interrogating the chemistry of a metallo-ligand.

From the perspective of the external atom (Cu, Zn) both complexes (Fig. 5) are four coordinate. The {(HL)Ni} moiety acts as a didentate ligand operating via the adjacent phenolates (O1, O2). The presence of a metal chelated into the phenolates would seem to have a marginal effect on the encapsulated nickel. It is curious that in neither complex does the pendant phenolate (O3) rotate into the coordination sphere of the external metal. This is especially so considering the structure of [{(HL)Zn}]ZnCl] (Fig. 6). Once again [6] the pKa of the phenols in these species is playing major role in the complexes which form.

The relationship between the motifs displayed by [{(HL)Ni]}$ZnBr_2$] and [{(HL)Zn]}ZnCl] was tested. An attempt to remove a halide and deprotonate the pendant phenoxide (O3 Fig. 7) was attempted using sodium hydroxide. Rather than rotate the phenoxide into the coordination sphere of the zinc, the complex dissociated. An attempt to construct a monohalide by limiting the stoichiometric amount of halide using [(HL)Ni]Br and zinc tetrafluoroborate was also unsuccessful, the major product obtained from solution being [{(HL)Ni]}$ZnBr_2$].

Having successfully placed a copper and zinc on the external face of [(HL)Ni] it was of interest to see if a similar result could be achieved with the "respective" copper and zinc complexes. The motifs displayed by copper namely [$\{(L)Cu\}Cu]_2^{2+}$ (Fig. 6) [$\{(HL)Cu\}_2Cu]^{4+}$ [5,6] would suggest that it should be possible to collect the phenolates in a manner which forms a chelating centre. However consistent with our studies on the lanthanoids we failed to isolate any dimetallic complexes derived from the nickel halides or nickel acetate. The reactions with zinc chloride confirmed this lack of reactivity as here we were able to isolate a charge separated salt namely [$(H_2L)Cu]^+$ Et_3NH^+ [$ZnCl_4]^{2-}$ (Fig. 8) which contained both metals.

The predominant products formed in the reactions with [$(H_2L)Cu$] were [$(H_2L)Cu$] itself. The crystallographic data base however, contains three complexes based on a modified [(Salpr)Cu] framework where different hydrated metal cations ($Cu(OH_2)_3$, $Co(OH_2)_3$ and $Mn(OH_2)_3$) are chelated to the phenolate donors [30]. These complexes display behaviour very similar to those which we report here (e.g. [(HL)Ni}$Ni(OAc)_2$], [(HL)Ni}$CuCl_2$] and [(HL)Ni}$ZnBr_2$]) and are related to those we have attempted to prepare here. This suggests that our problems with the preparation of the copper complexes may rest with our synthetic design. In contrast, the products obtained from the treatment of [$(H_2L)Zn$] with nickel and copper are [$(H_2L)Ni$] and [$(H_2L)Cu$], respectively. This suggests that a metal replacement reaction had taken place for the zinc precursor. In retrospect this is a possible problem with the design of mixed metal complexes of this type when the second metal centre being introduced onto the external sites of the complex has a higher formation constant for the N_4 donor set in the interior of the ligand. In certain instances where the exchange rates are favourable and the ligand is flexible, metal exchange can be expected to be a competing reaction. A related process is believed to be central to the synthesis of the mixed nickel lanthanoid complexes ([$\{(L)Ni\}_2Ln(HOMe)]^+$, Fig. 1) and responsible for the removal of the zinc during the synthesis of [$\{(L)Ce\}_2$-μO_2] from [$(H_2L)Zn$] [6].

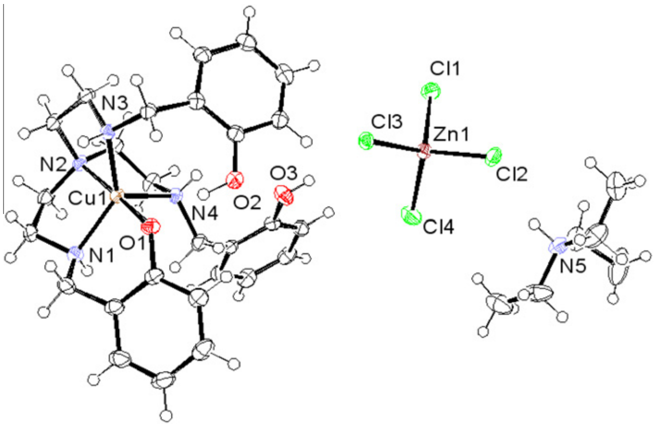

Fig. 8. The X-ray crystal structure of [$(H_2L)Cu]^+$ Et_3NH^+ [$ZnCl_4]^{2-}$. The thermal ellipsoids are drawn at 50% probability.

4. Concluding remarks

The systematic construction of complexes which utilise [(H_xL)M] as a ligand is a partial success. Metals such as nickel and zinc have been successfully encapsulated. We are still unable to achieve this aim with copper most likely due to the design of the ligand and the preferred geometry of the metal centre. Placing metals on the outer face of these ligands has also been a partial success. Copper sits didentate and zinc sits both didentate and tridentate to these metallo-ligands. However, there remains some problems with controlling the ultimate positions of the metals especially when using {(H_2L)Zn] as a ligand.

Acknowledgments

AM would like to express his gratitude to Kano University of Science and Technology, Wudil, Nigeria for financial assistance. JR acknowledges the EPSRC national crystallography service at the University of Southampton for data collection on three compounds.

Appendix A. Supplementary data

CCDC 788756, 788757, 788758, 788759, 788760, 788761 and 788762 contain the supplementary crystallographic data for this paper;. These data can be obtained free of charge via http://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 e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.03.004.

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