The nickel, copper and zinc complexes of a potentially heptadentate nitrogen donor ligands.

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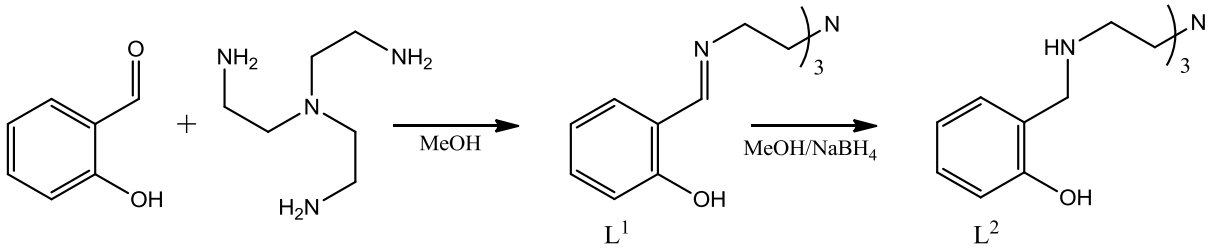
Abbreviations

Tren: tris-(2-aminoethyl)amine
L^1: tris-(2-hydroxybenzylidene)aminoethylamine
$L^{2:}$ tris-(2-hydroxybenzyl)aminoethylamine
L^3: tris-(2-aminobenzylidene)aminoethylamine
L^4: tris-((2-aminobenzyl)aminoethylamine

Abstract

The synthesis of the potentially heptadentate ligands, tris-(2-aminobenzylidene)amino-ethylamine (L^3) and tris-(o-aminobenzyl)aminoethylamine (L^4) are reported. Complexes of L^3 with nickel copper and zinc have been synthesised and characterised. However, the nickel and zinc compounds are observed to re-arrange during the procedures used to produce samples for X-ray diffraction analysis. In both cases aniline groups are found to migrate to give rise to unique but related coordinated polyamine species. A rational route which allows for the reduction of the imine function in L^3 is presented giving rise to a heptadetate ligand (L^4) which contains primary, secondary and tertiary amines. Having removed the reactive imine function, the synthesized nickel and copper complexes follow the expected synthetic and structural pattern with the nickel complex being observed to be octahedral and the copper(II) complex five coordinate. The zinc complex is in contrast different. As observed for L^3, it is possible to generate simple ZnL^3 complexes but these are prone to intramolecular cyclisation where an aniline nitrogen couples with the secondary amine to form a coordinated indizine.

Introduction



Scheme 1

Multidentate phenolate ligands derived from tris-(2-aminoethyl)-amine (tren) and salicylaldehyde (L^1, L^2) have been known for over fifty years (scheme 1) [1, 2]. The early chemistry of these ligand systems was undoubtedly hindered by the inability to crystallographically characterise the products as many of the complexes generated are multimetallic in nature [2-14]. Indeed one of the fascinating aspects of this chemistry are the myriad of motifs which can be produced by challenging a potentially heptadenate ligand with transition metals with a preference for low coordination numbers. With divalent metals the primary complexes produced in combination with L^1 and L^2 are anionic and are thus capable of acting as ligand themselves and this gives rise to a related series of multimetallic and heterometallic complexes [2-14]. Many of these have interesting magnetic properties [7, 9, 14]. Replacing the phenol residue with an aniline moiety is a simple way of increasing the versatility of this family of ligands [15]. Multidentate nitrogen donor ligands have been identified as central to the design and function of ruthenium complexes for water oxidation catalysis and as models for nitrogen rich donor sites in metalloenzymes [16, 17]. In the belief that the metal complexes of the amine analogues of L^1 and L^2 (figure 1) might also have a rich and diverse chemistry we have sought to identify simple routes into their synthesis. Our previous studies using L^1 and L^2 have shown that the divalent metals cations such as nickel, copper and zinc generate a wide range of structural motifs and as such we have adopted these metals again to explore the behaviour of these two heptadentate nitrogen donor ligands (L^3, L^4 figure 1).

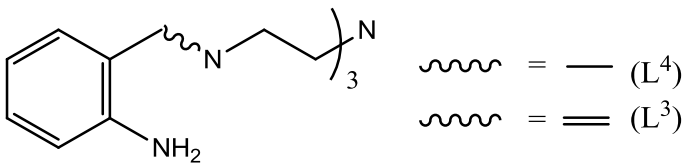


Figure 1. A schematic representation of tris-(2-aminobenzylidene)aminoethylamine (L^3) and tris-((2-aminobenzyl)aminoethylamine (L^4).

Experimental

All experiments were carried out using standard apparatus and commercially available chemicals**.** O-aminobenzaldehyde was prepared as previously reported [18]. NMR analysis was carried out on a Bruker AMX 400 operating at 400 MHz for ^{1}H for proton and 100 MHz for ^{13}C. Solid reflectance spectra (400 – 900 nm) were recorded on a Photonics CCD array UV-Vis spectrophotometer. Mass spectra were recorded in house on a Thermo Finnigan LCQDuo by electrospray ion trap (4.5 kW, 200 ^{o}C). Infra red spectra were recorded using an A2 technologies ATR FT-IR spectrometer. Elemental microanalysis was carried out in house on a Perkin Elmer 2400 CHN Analyser.

X-Ray measurements were conducted using a Nonius Kappa CCD diffractometer at 123 K using graphite monochromated Mo-Kα radiation. Crystals were coated in mineral oil and mounted on glass fibers. The heavy atom positions were determined by Patterson methods and the remaining atoms located in difference electron density maps. Full matrix least-squares refinement was based on F2, with all non-hydrogen atoms anisotropic. While the hydrogen atoms were mostly observed in the difference maps, they were placed in calculated positions riding on the parent atoms except those involved in hydrogen bonding which were refined isotropically. The structure solution and refinement used the programs SHELXL SHELXL-97 [19] and the graphical interface WinGX [20]. A summary of the crystallographic parameters is given in Table 1.

Synthesis of tris-((2-aminobenzylidene)-aminoethylamine (L^3): o-amino-benzaldehyde (0.66 g, 5.5 mmol) was refluxed with tris(2-aminoethyl)amine (0.3 g, 2.0 mmol) in methanol (50 ml) for 90 minutes. The pale yellow solution produced was reduced in volume to 10 ml. Diethyl-ether (20 ml) was added to obtain a white solid which was suction filtered and dried. The solid was recrystallised from chloroform and methanol by vapour diffusion. Yield 67%. m.p. 136^{o}C. Anal. Found: C, 70.26; H, 8.18; N, 20.92 % Calcd. for $C_{27}H_{33}N_{7}.1/2CH_3OH$: C, 70.03; H, 7.48; N, 20.78 %. ^{1}H NMR (400 MHz, $CDCl_3$; δ): 8.2 (s, 1H, -HC=N), 7.1 (t, 1H, arom); 6.8 (d, 1H, arom); 6.6 (m, 2H, arom); 6.3 (br s, 2H, -NH_2); 3.6 (t, 2H, -CH_2-); 3.5 (s, MeOH); 2.8 (t, 2H, -CH_2-). ^{13}C-{^{1}H} NMR (100 MHz $CDCl_3$; δ): 165, 148, 134, 131, 118, 116, 115, 60, 56. ν/cm^{-1}: 3231 (NH), 1639 (C=N), 1588 (C=C), 753 (arom). MS (ESI, *m/e*): 456 (100%),

Synthesis of tris-(2-aminobenzyl)aminoethylamine (L^4): Tris-(2-aminoethyl)amine (2 g, 13.7 mmol) and 2-nitrobenzaldehyde (6.2 g, 41 mmol) were refluxed in methanol (50 ml) for 1 hour. The solution was allowed to cool and the orange solid, (L^{4A}), collected by filtration (Yield 89%).

L^{4A} was re-dissolved in methanol (50 ml) and treated with $NaBH_4$ (1.5 g, 43 mmol) over a 1 hr period under the blanket of nitrogen. The yellow solution was allowed to stir overnight. The solvent was removed under reduced pressure to give an orange oil. An aqueous solution of ammonium acetate (4g in 50 ml) was added to the oil and the mixture extracted with chloroform (3 x 100 ml). The chloroform solution was dried over anhydrous Na_2SO_4, filtered and the solvent reduced in volume to give a yellow solid. The yellow solid (L^{4B}), collected by filtration (Yield 68%).

L^{4B} produced above was suspended water (175 ml) and conc. hydrochloride acid (0.5 ml) in a 500ml round bottom flask containing $FeSO_4.7H_2O$ (105 g, 0.38 mmol). The mixture was heated to 90^{o}C followed by the addition of conc. ammonia solution (30 ml). The black slurry was stirred while being allowed to cool (~ 1 hr). The mixture was extracted with chloroform (3 x 100 ml), dried over anhydrous Na_2SO_4, filtered and the solvent removed to give a viscous yellow oil (L^4). Yield 54%.

Alternatively the L^{4B} produced above was dissolved in propan-2-ol and palladium on carbon (10%) (200 mg) was added. The suspension was heated with stirring to 50^{o}C and hydrazine hydrate (15 ml) added dropwise. The reaction mixture was heated to reflux for 2 hours under nitrogen before being filtered and the solvent removed in vacuo to yield L^4 as a viscous yellow oil. Yield 75%.

L^{4A}: Anal. Found: C, 59.45; H, 5.48; N, 18.34 % Calcd. for $C_{27}H_{27}N_7O_6$: C, 59.44; H, 4.99; N, 17.94 %. ^{1}H NMR (400 MHz, $CDCl_3$; δ): 8.6 (s, 1H, -HC=N), 8.0 (dd, 1H, arom), 7.9 (dd, 1H, arom); 7.6 (dt, 1H, arom); 7.5 (dt, 1H, arom); 3.8 (t, 2H, -CH_2); 3.0 (t, 2H, –CH_2-). ^{13}C-{^{1}H} NMR (100 MHz $CDCl_3$; δ): 157, 133, 131, 130, 129, 124, 69, 55, 31. ν/cm^{-1} 1630, 1575, 1525, 1340, 740. MS (ESI, *m/e*): 546 (100%),

L^{4B}: ^{1}H NMR (400 MHz, $CDCl_3$; δ): 7.9 (d, 1H, arom), 7.6 (d, 1H, arom); 7.5 (t, 1H, arom); 7.4 (t, 1H, arom); 4.0 (s, 2H, -CH_2-); 2.7 (t, 2H, -CH_2-), 2.6 (t, 2H, –CH_2-). ^{13}C-{^{1}H} NMR

(100 MHz $CDCl_3$; δ): 149, 136, 133, 131, 128, 124, 54, 50, 47. ν/cm^{-1} 1520, 1340, 725. MS (ESI, *m/e*): 552 (100%),

L^4: ^1H NMR (400 MHz, $CDCl_3$; δ): 7.3 (br s, 2H, arom), 7.0 (d, 1H, arom); 6.6 (d, 1H, arom); 4.5 (br s, 2H, -NH_2); 3.7 (s, 2H, -CH_2-); 2.6 (br s, 2H, -CH_2-), 2.5 (br s, 2H, –CH_2-) 1.5 (br s, 2H, -NH). ^{13}C-{^1H} NMR (100 MHz $CDCl_3$; δ): 147, 129, 128, 124, 117, 115, 54, 53, 47. MS (ESI, *m/e*): 462 (100%),

Schiff Base Chemistry

Synthesis of nickel, copper and zinc complexes of L^3: L^3 (0.05 g, 0.11 mmol) dissolved in methanol (15 ml) was treated with 2 mol equivalents of the relevant metal halide. The mixture was stirred at 50°C for 15 minutes, allowed to cool and filtered.

[NiL^3] 2Cl: Anal. Found: C, 52.79; H, 6.08; N, 15.41% Calcd. for $C_{27}H_{33}N_7NiCl_2.2H_2O$: C, 52.21; H, 6.00; N, 15.78 %. FTIR [(ν/cm-1 (KBr)]: 2925 (-NH_2), 1610 (-C=N), 1500 (C=C), 760 (arom). MS (ESI, *m/e*): $[M-H]^+$ 512 (25%), $[M+R+H]^+$ 615 (25%) $[M+2R+H]^+$ 718 (100%), $[M+3R+H]^+$ 823 (10%), $[M-R+H]^+$ 409 (10%) $[M-2R+H]^+$ 306 (25%), R = anilino group. These are observed to migrate during the mass spectroscopic analysis

[NiL^3] 2I: Anal. Found: C, 44.83; H, 5.11; N, 14.65% Calcd. for $C_{27}H_{33}N_7I_2Ni$: C, 42.22; H, 4.33; N, 12.76 %. FTIR [(ν/cm-1 (KBr)]: 2925 (-NH_2), 1610 (-C=N), 1500 (C=C), 760 (arom). $[M-H]^+$ 512 (10%), $[M+3Na-2H]^+$ 581 (35%) $[M+R-2H]^+$ 684 (15%), $[M+2R-2H]^+$ 787 (100%). R = anilino group. These are observed to migrate during the mass spectroscopic analysis. The poor agreement of the microanalysis is believed to stem from the partial decomposition of the product.

Crystals suitable for X-ray diffraction were obtained from the very slow evaporation of a methanol solution of [(L^3)Ni][I_2]. The crystals were taken from an oily residue in the base of the flask which mitigated against further analysis.

[CuL^3] 2Cl: Anal. Found: C, 53.15; H, 5.98; N, 15.49% Calcd. for $C_{27}H_{33}N_7CuCl_2.H_2O$: C, 53.33; H, 5.80; N, 16.12 %. FTIR [(ν/cm^{-1} (KBr)]: 2925 (-NH_2), 1615 (-C=N), 1505 (C=C),

760 (arom). MS (ESI, *m/e*): $[M-H]^+$ 517 (25%), $[M+2R-H]^+$ 723 (45%) $[M-2R+2H]^+$ 310 (100%), λmax = 595 (solid)

$[ZnL^3][ZnCl_4]$: Anal. Found: C, 42.51; H, 4.98; N, 12.60 % Calcd. for $C_{27}H_{33}N_7Zn_2Cl_4.2H_2O$: C, 42.43; H,4.87; N,12.83 %. FTIR [(ν/cm^{-1} (KBr)]: 2800-3200 (-NH_2), 1610 (-C=N), 1495 (C=C), 760 (arom). MS (ESI, *m/e*): $[M-H]^+$ 518 (30%), $[M-2H-2R]^+$ 310 (100%). ^1H NMR (400 MHz, $CDCl_3$; δ): 7.02 (s, 1H, -CH=N), 7.00 (s, 1H, -CH=N), 6.92 (d, 1H, arom), 6.9 (s, 1H, -CH=N), 6.88 (d, 1H, arom); 6.6-6.4 (m, 10H, arom); 3.7 (br s, 2H, -NH_2); 3.3 (br s, 4H, -NH_2); 2.7-2.5 (m, 12H, -CH_2-).

Zinc crystals were grown by slow evaporation of the mother liquors over 24 hours leading to a ligand rearrangement.

$[ZnL^3][ZnCl_4]$: Anal. Found: C, 42.51; H, 4.98; N, 12.60 % Calcd. for $C_{27}H_{33}N_7Zn_2Cl_4.2H_2O$: C, 42.43; H,4.87; N,12.83 %. FTIR [(ν/cm^{-1} (KBr)]: 3440 (-NH_2), 1650 (-C=N), 1495 (C=C), 760 (arom). MS (ESI, *m/e*): 518 (100%), 259 (55%).

Secondary Amine Chemistry

Synthesis of (tris-(2-aminobenzyl)-aminoethylamine) nickel) nitrate: L^4 (0.07 g, 0.16 mmol) was dissolve in methanol (20 ml). The mixture was stirred at 50°C followed by addition of $NiNO_3.6H_2O$ (0.045 g, 0.16 mmol). The brown solution was stirred for a further 10 minutes, allowed to cool and filtered. Crystals (deep lilac) were grown by slow evaporation of the saturated methanol solution. Yield 73%. Anal. Found: C, 50.54; H, 6.05; N, 19.57 % Calcd. for $C_{27}H_{39}N_9NiO_6$: C, 50.33; H, 6.10; N, 19.56 %. ν/cm^{-1} 2960, 1600, 1500, 1380, 760. MS (ESI, *m/e*): 518 (100%), λmax (solid) 550 (shoulder) 940.

Synthesis of (tris-(2-aminobenzyl)-aminoethylamine)-nickel) chloride: L^4 (0.053 g, 0.11 mmol) and nickel chloride hexahydrate (0.023 g, 0.1 mmol) were dissolved separately in the minimum amount of ethanol. The solutions were filtered and the solution of L^4 added to the nickel solution. The mixture was stirred for 1 hr whereupon the solution turned green and a yellow/green precipitate formed. This was collected by filtration and washed with diethyl-ether. Yield 50%. Anal. Found: C, 47.66; H, 5.96; N, 14.92%. Calcd. for

$C_{27}H_{39}N_9NiCl_2.5H_2O$ C, 47.60; H, 7.25; N, 14.39 %. ν/cm^{-1} 2960, 1600, 1500, 1310 (NO_3) MS (ESI, *m/e*): 259 (M^{2+} 100%), 518 (M^+ 100%), 554 ($[M+Cl]^+$ 65%), 593 ($[M+Cl+K]^+$ 64%), 632 ($[M+Cl+2K]^+$ 40%), λmax (solid) 620 nm.

Synthesis of (tris-(2-aminobenzyl)-aminoethylamine)-copper) nitrate: L^4 (0.050 g, 0.11 mmol) and copper nitrate trihydrate (0.025 g, 0.1 mmol) were dissolved separately in the minimum amount of acetonitrile. The solutions were filtered and the solution of L^4 added to the copper solution. The mixture was stirred for 1 hr whereupon the solution turned dark green and a green precipitate formed. This was collected by filtration and washed with diethyl-ether. Yield 75%. Anal. Found: C, 45.26; H, 5.29; N, 17.80%. Calcd. for $C_{27}H_{39}N_9CuO_6.4H_2O$ C, 44.97; H, 6.57; N, 17.48 %. ν/cm^{-1} 2960, 1600, 1500, 1380, 1310 (NO_3), 750. MS (ESI, *m/e*): 523 (M^+ 25%), 519 ($[M-4H]^+$ 100%), 5154 ($[M-8H]^+$ 64%), ($[M+Cl+2K]^+$ 40%), λmax (solid) 620 nm.

Synthesis of (tris-(2-aminobenzyl)-aminoethylamine)-copper) chloride: L^4 (0.053 g, 0.11 mmol) and copper chloride dihydrate (0.023 g, 0.1 mmol) were dissolved separately in the minimum amount of ethanol. The copper solution was added to the solution of L^4. The mixture was stirred for 30 mins during which time the solution turned deep green and a precipitate formed. This solid was collected by filtration and washed with diethyl-ether. Yield 40%. Anal. Found: C, 50.13; H, 6.47; N, 13.87 % Calcd. for $C_{27}H_{39}N_7CuCl_3.EtOH.H_2O$: C, 50.00; H, 6.94; N, 14.07 %. ν/cm^{-1} 2925, 1620, 1495, 1445, 755. MS (ESI, *m/e*): 555, 557 (100%) $[M+OMe]^+$, 571, 573 (100%) $[M+OEt]^+$, λmax (solid) 665.

Crystals (green) of $[CuL^4H]$ 3Cl were grown by diffusion at the interface of a propanol solution of copper chloride with that of L^4 also in propanol.

Synthesis of tris-(2-aminobenzyl)-aminoethylamine)-zinc salts: L^4 (0.053 g, 0.11 mmol) and zinc salt (chloride/ nitrate, 0.1 mmol) were dissolved separately in the minimum amount of ethanol. The solutions zinc solutions were added to the solution of L^4. The mixture was stirred for 30 mins during which time the creamy solution turned yellow and a precipitate formed. This solid was collected by filtration and washed with diethyl-ether.

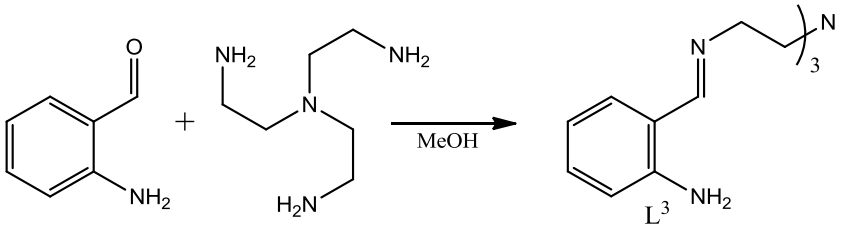
[ZnL^4] $2NO_3$: Yield 25%. Anal. Found: C, 46.11; H, 5.15; N, 17.98%. Calcd. for $C_{27}H_{39}N_9O_6Zn.3H_2O$ C, 46.00; H, 6.43; N, 17.88 %. ν/cm^{-1} 2960, 1620, 1480, 1315 (NO_3), 1035, 755. MS (ESI, *m/e*): 524 ($M\text{-}H^+$ 100%).

[ZnL^4] $ZnCl_4$: Yield 25%. Anal. Found: C, 44.30; H, 4.74; N, 13.35%. Calcd. for $C_{27}H_{39}N_7Zn_2Cl_4$, 44.17; H, 5.35; N, 13.35 %. ν/cm^{-1} 2960, 1620, 1480, 1035, 750 524 MS (ESI, *m/e*): 524 ($M\text{-}H^+$ 30%), 520 ($M\text{-}5H^+$ 30%), 516 ($M\text{-}9H^+$ 30%).

	L^3	"NiL^2" H_3O^+ 3I	"ZnL^2" $[ZnCl_4]^{2-}$	NiL^4 $2NO_3$	$CuHL^4$ Cl_3 $0.5C_3H_7OH$	
Empirical Formula	$C_{27}H_{35}N_7O$	$C_{21}H_{35}I_3N_6NiO_2$	$C_{27}H_{36}Cl_4N_7O_{1.50}Zn_2$	$C_{27}H_{39}N_9NiO'$	$C_{31.5}H_{52}Cl_3CuN_7O_{1.5}$	$C_{27}H_{35}N_9O_6Zn$
FW	473.62	842.96	755.17	644.38	722.69	647.01
Crystal system	trigonal	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	R-3	P-1	P21/n	P21/c	P21/n	P21/c
a / Å	12.9828(4)	9.8973(3)	9.4360(6)	10.2682(3)	9.5888(8)	18.053(3)
b / Å	12.9828(4)	10.8803(5)	16.0009(8)	15.9820(5)	27.554(4)	17.308(3)
c / Å	26.1704(10)	14.5836(6)	20.7248(11)	18.1017(5)	14.073(2)	20.711(3)
α / deg	90.00	69.044(4)	90.00	90	90	90
β / deg	90.00	79.799(3)	98.967(2)	90.552(2)	93.715(10)	94.408(7)
γ / deg	120.00	89.366(3)	90.00	90	90	90
Z	6	2	4	4	4	8
V / $Å^3$	3820.1(2)	1441.05(10)	3090.9(3)	2970.47(15)	3710.4(8)	6452.2(18)
μ_{calc} / mm^{-1}	0.079	3.915	1.935	0.710	3.096	0.814
No. Rflns Measd	9712	13150	11637	31226	12064	36271
No. Unique reflns	1854	6889	6060	6468	5453	10091
No Observed	1567	6047	3419	4227	2674	4224
No. parameters	122	329	399	439	420	780
R^a ($I > 2\sigma(I)$)	0.1338	0.072	0.1410	0.081	0.266	0.078
R_w^b (all reflns)	0.0513	0.028	0.0634	0.039	0.089	0.208
GOF	1.083	1.063	1.038	0.934	1.006	0.954

Table 1. Crystallographic data. The crystallographic data for $CuHL^4$ $Cl_3.0.5C_3H_7OH$ is poor, with the structure not refining to an acceptable solution. The cell dimensions etc obtained are however, included here for completeness.

Results and Discussion.



Scheme 2

L^3 was prepared from the tris(aminoethyl)amine and o-amino-benzaldehyde (scheme 2). It was isolated as an off-white solid which could be crystallised from chloroform-methanol (figure 2). Consistent with Garcia et al. [15], structural analysis of L^3 reveals that the three anilino groups are folded inwards from the apical nitrogen such that the three aryl rings are placed in close proximity to one another. The distance between the rings (e.g. H5-C1; 2.902 Å) suggests that an interaction of the ring hydrogens with the π-system has an influence in stabilising the structure. The anilino hydrogens are also directed towards the Schiff base nitrogens (N2-H2N1; 2.027 Å) thus forming a network of three internal hydrogen bonds.

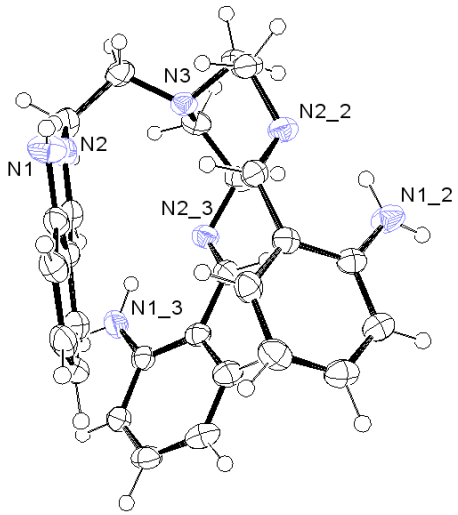
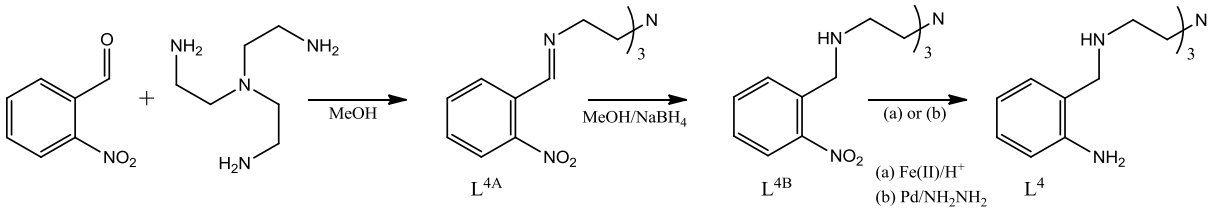


Figure 2. The X-ray crystal structure of tris-((2-aminobenzylidene)-aminoethylamine. The thermal ellipsoids are drawn at 50% probability. This structure has been previously reported by Garcia et al. [15]. The structure was re-determined for this study because of the re-arrangements discussed below

The synthesis of the reduced multidentate nitrogen ligands such as L^1 (Scheme 1) typically commences by condensing the relevant aldehyde with tren. The resulting Schiff base is then reduced with sodium borohydride. Consistent with the report of McKee et al, we could synthesis the required Schiff base using tren and o-amino-benzaldehyde (scheme 2) [21].

However, the subsequent total reduction of the imine and nitro groups using either borohydride or aluminium hydride was unsuccessful. We thus altered the synthetic strategy. The Schiff base derived from o-nitro-benzaldehyde with tren was first produced (Scheme 3). This was subsequently reduced using sodium borohydride to form the corresponding secondary amine. Subsequently, the nitro group was reduced using acidic ferrous sulfate or hydrazine over the palladium to produce the desired polyamine ligand (L^4) which was obtained as a viscous oil [16].* The reaction is presented in the experimental as three independent steps and during the development of the synthesis of the polyamine we took care to isolate the various intermediates. In practice, however, it is possible to carry out the first two steps of the synthesis (coupling and reduction) in sequence. Similarly the reduction of the nitro group to give the desired polyamine can be achieved using the crude liquors obtained by simply taking the products of imine reduction to dryness.



L^{4A} L^{4B} L^4

Scheme 3

The Schiff base chemistry of L^3

The halides of nickel, copper and zinc were treated with L^3 under conditions typically employed (methanol ~65 ºC for 2 hrs.) for the formation of the related salicylaldehyde Schiff base species [6, 7]. The mass spectra of the isolated complexes are dominated by ions associated with the parent species (ML^3) and their fragmentation/recombination products. We could find no evidence to support the formation of multimetallic species at this juncture (c.f. $M_3(L^1)_2$, M = Ni, Zn; $Cu_4(L^1)_2$) [6]. Vibrational spectroscopy of the three complexes (coincident amide, imine and aromatic bands) indicates that the structures of these products are of high symmetry and related. It was possible to record the ^{1}H NMR spectrum of the ZnL^3 which shows that there are three imine environments (δ7.00, δ7.02, δ6.90). However, the chemical shift difference is not sufficient to suggest that any of these remain uncoordinated. The region assigned to tren is broad but compact indicative that the imines are all coordinated and chemically similar. Thus it can be proposed that ZnL^3 is a simple six coordinate species (c.f. $Zn_3(L^1)_2$) [6].

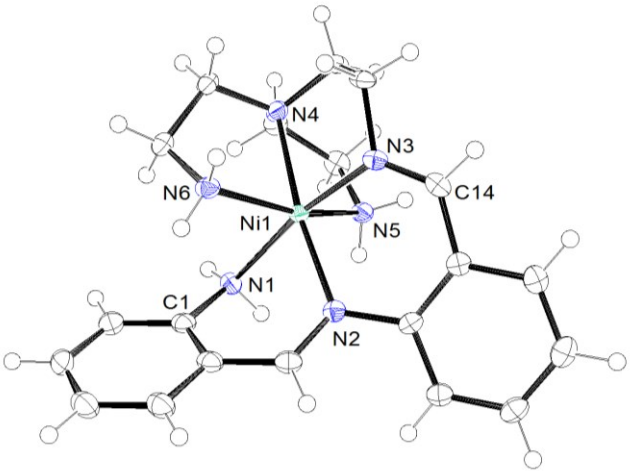


Figure 3. The X-ray crystal structure of the isolated adduct of nickel iodide and L^3. The structure is presented to clearly show the fused aniline moieties which results from Schiff base cleavage/migration. Selected bond lengths (Å): Ni-N1, 2.186(3); Ni-N2, 2.087(3); Ni-N3 2.018(3); Ni-N4, 2.121(3); Ni-N5, 2.093(3); Ni-N6, 2.123(3). Bond angles (°) N1-Ni-N2, 81.95(11); N1-Ni-N3, 170.28(11); N1-Ni-N4, 106.19(11); N1-Ni-N5, 87.43(11); N1-Ni-N6, 88.05(11); N2-Ni- N3, 88.58(11); N2-Ni-N4, 171.74(11); N2-Ni-N5, 98.92(11); N2-Ni-N6, 100.65(10), N3-Ni-N4, 83.24(11); N3-Ni-N5, 91.97(11); N3-Ni-N6, 95.83(11); N4-Ni-N5, 80.34(11); N4-Ni-N6, 81.34(10); N5-Ni-N6, 159.08(11). The thermal ellipsoids are drawn at 50% probability.

Previous studies clearly show that it is difficult to predict the absolute structures of the metal complexes of heptadentate ligands such as those discussed here. Thus, in an effort to gain greater insight into the structure of these ML^3 species we extending the scope of the study to a range of salts. From the reactions with nickel iodide we were able to obtain suitable crystals for analysis by diffraction methods (figure 3). The structure obtained is, however, not consistent with that expected for a simple ML^3 complex. It would seem that the protracted crystallisation process has allowed the ligand to both hydrolyse and re-arrange. Not only is one of the aniline units lost completely a second is transferred to an adjacent aniline group, probably via an intramolecular reaction, giving rise to the formation of a coordinated aniline-methylidene-aniline moiety. The resulting perturbation of the number (seven to six) and positioning of the aniline donors facilitates the movement of the nickel into the coordinating environment of all four donors on tren (c.f. NiL^2). [11, 13]. Migrations and rearrangements of this type go some way to explaining the behaviour of the parent species in the mass spectrometer [22, 23] where ions with masses consistent with the gain and loss of aniline units are freely seen. Although not as prominent a similar degradation process has been reported for the nickel salts of L^1 where the phenolate arms are lost [6]. Consistent with the observation reported here, the reaction reported takes time to come to completion.

In the reactions involving zinc chloride a second product crystallised directly from the cooling mother liquors (figure 4). On analysis by XRD methods we observed that the ligand (L^3) has re-arranged within the lifetime of the crystallisation process. Consistent with the nickel example above (figure 3) an intermolecular migration has occurred whereby the aniline group migrates to replace the nitrogen of tren in the Schiff base linkage. However, in this instance a second coupling takes place and in-so-doing forms a tetracyclic ring system fused to a nitrogen donor on tren (N4, figure 4). As the reaction proceeds the zinc migrates deep into the tren moiety maintaining a coordination number of 5. This more complex rearrangement is most likely a result of the increased Lewis acidity of zinc.

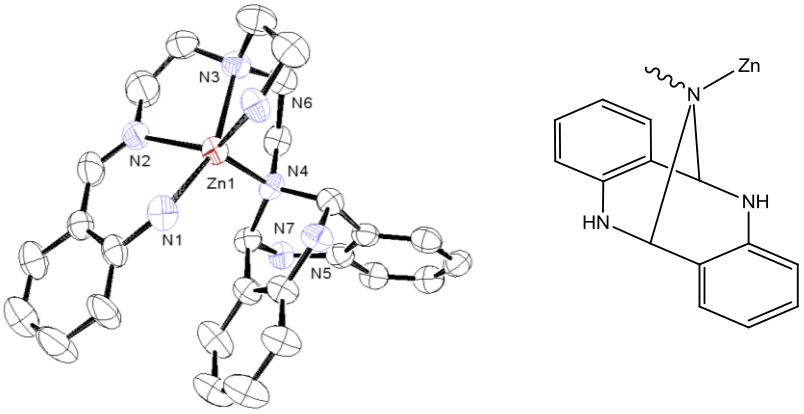


Figure 4. Left: The X-ray crystal structure of the isolated adduct of zinc chloride and L^3. The structure is presented to clearly show the fused tetracyclic component of the ligand which results from Schiff base cleavage/migration. Right: A schematic representation of the fused aniline moieties. The solvent of crystallisation, protons and $[ZnCl_4]^{2-}$ have been omitted for clarity. The thermal ellipsoids are drawn at 50% probability.

In both instances (nickel and zinc) we have evidence that the primary complex (ML^3) forms with ease. Structural analysis of the ligand itself (re-determined, figure 2) clearly shows that the components are positioned in line with the expected condensation reaction [15]. Thus, migration must be occurring as a result of the placement of the Lewis acid at the various donors. The hypothesis is that nickel, by virtue of its preferred higher coordination number, only facilitates the coupling of two aniline groups. Zinc however is both a slightly stronger Lewis acid and has a lower coordination number. This raises the prospect of a more aggressive ring closure reaction and one which has the capacity to encompass further aniline units. Although the Schiff base linkage remains an integral part of many ligand designs, researchers tend to dismiss or fail to consider the reactivity of the imine function in the long, or as is shown here, the short term. Our pervious attempts to generate heptadentate N_4S_3 ligand system based on tren and 2-(*tert*-butylthio)benzaldehyde where curtailed due to the

limited stability of the imine group within the metal complexes studied [24]. The salicylidene-tren systems are more robust but even these, when metallated (e.g. nickel) have demonstrated a tendency to degrade all-be-it over a prolonged time period [6]. In retrospect is thus unsurprising that the nitrogen donor systems reported here display behaviour intermediate between that observed for the phenolates and thio-ethers.

Secondary amine chemistry (L^4).

The reaction of tris-((2-aminobenzyl)aminoethylamine (L^4) with nickel nitrate gives rise to a purple material which could be crystallographically characterised. X-ray analysis revealed this to be the desired six-coordinated complex (figure 5) where the nickel sits deep in the hepta-dentate ligand coordinating to the tertiary amine (N2 figure 5) and the three secondary amines (N1, N3, N4). The coordination sphere is then completed via the use of two of the anilino groups. Thus the observed structure of this tripodal anilino- ligand follows that of the related tripodal phenolate (table 2) in that the geometry at nickel is best described as distorted octahedral [11, 13]. We were unable to grow crystals of the corresponding chloride species. However, spectroscopic and elemental analysis support the view that the nickel cation ($[Ni(L^4)]^{2+}$) in this species is, as expected, the same as that formed in the reaction with nickel nitrate.

The reaction of copper chloride and nitrate with L^4 produced products which vibrational and mass spectroscopies again confirms contain the same complex cation ($[Cu(L^4)]^{2+}$). These products steadfastly refused to crystallise using traditional recrystallisation procedures and we eventually grew a poor quality crystal by the slow diffusion of a solution of copper(II) chloride in propanol into a solution of L^4 in propanol (figure 5). The resulting structure did not refine to an acceptable point and as such the data can only be used to confirm the gross structure of the complex i.e. that the adduct is again a simple 1:1 complex. Once again this motif follows the established chemistry of the phenolate analogue where the copper sits in a five coordinate environment using the secondary and tertiary amines derived from tren as the primary donors. In this instance only one of the aniline groups are incorporated into the metal coordination sphere. Progressing to zinc we obtained yellow complexes which analysed for $[ZnL_4]^{2+}$. Although we were unable to confirm a structure using X-ray methods, vibrational and mass spectroscopies indicate that the $[ZnL_4]^{2+}$ motif is iso structural with for $[CuL_4]^{2+}$.

This behaviour is in line with the corresponding chemistry of the secondary amine tren-based, N_4O_3-donor ligands (L^2).

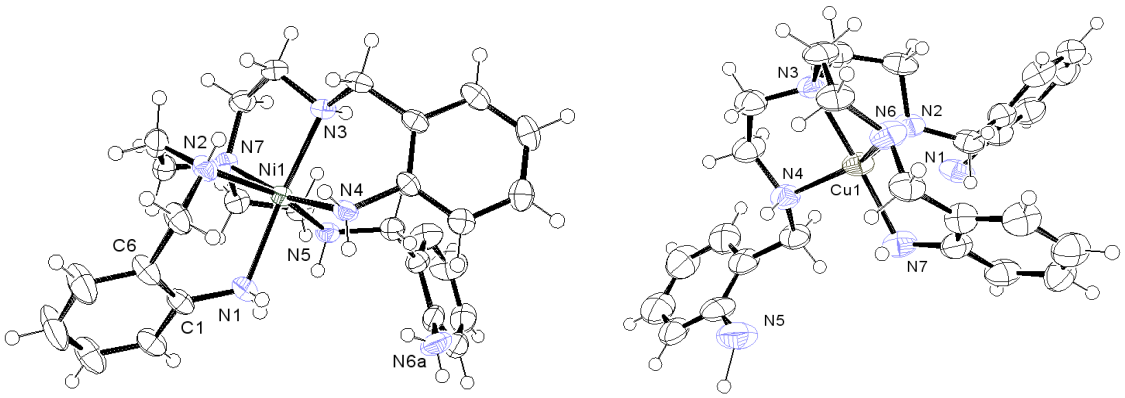


Figure 5. The molecular structures of left: $[Ni(L^4)]$ $2NO_3$ and right: $[Cu(HL^4)]$ 3Cl. Three chlorides are found in the lattice of $[Cu(HL^4)]$ and consequently it is believed that one of the aniline moieties must be protonated. The nitrates and chlorides are not shown for clarity. The key metrical parameter for $[Ni(L^4)]$ $2NO_3$ can be found in table 1. The thermal ellipsoids are given at 50% probability. The crystallographic data for $CuHL^4$ $Cl_3.0.5C_3H_7OH$ is poor, with the structure not refining to an acceptable solution. The picture shown serves only to demonstrate the connectivity of the atoms.

	trans N2-M-D	M-N2	M-N (sec amines)	M-D (D = NH_2, O)
$[Ni(L^4)]^{2+}$ D = NH_2 (aniline)	167.77	2.103	2.135, 2.171, 2.154	2.145, 2.205
$[Ni(L^2)]^{2+}$ D = OH (phenolate)	175.11	2.102	2.138, 2.062, 2.128	2.189, 2.005

Table 2. The metrical parameters for $[Ni(L^4)]^{2+}$ and $[Ni(L^2)]^{2+}$. The distances associated with the tren moieties would seem to be conserved between the two ligand systems (N_4O_3; N_7) [11, 13]. The crystallographic data for $CuHL^4$ $Cl_3.0.5C_3H_7OH$ is poor, with the structure not refining to an acceptable solution. It is not possible to quote accurate metrics for this species.

The complexes of L^4 were all prepared by the addition of a metal salt to ligand without heating in such a manner that sufficient product precipitated quickly from the mother liquors. This crude approach was adopted as there was evidence that the complexes did not survive excessive heating in solution even at modest temperatures (e.g. methanol for 1 hr). The products formed under these reactions gave inconsistent results, but mass spectroscopic evidence shows clear signs that the molecular weight of the ions was lower than desired. During our attempts to isolate crystals for analysis by X-ray diffraction methods, compounds were re-dissolve in a minimum amount of methanol and the samples left to evaporate. This methodology was successful in the isolation of the crystals of $[NiL^4]^{2+}$ (figure 5). However,

although we were able to isolated crystals suitable for X-ray diffraction from the solution containing [ZnL^4] 2[NO_3], the complex isolated for analysis was one in which the ligand (L^4) had rearranged (figure 6). Here one of the aniline moieties and secondary amines come together in a ring closing reaction which gives rise to a coordinated indazole (figure 6). The transformation requires the loss of two mole equivalents of hydrogen and reduces the denticity of the ligand from hepta- to hexa- dentate.

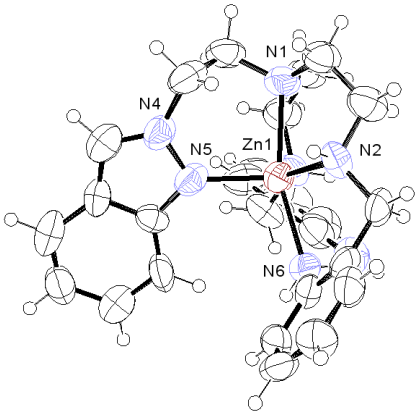


Figure 6 The XRD structure of the material obtained from the slow evaporation of [ZnL^4] 2[NO_3] from methanol. The structure is present in a manner which shows the formation of the indazole ring The nitrates are not shown for clarity. The thermal ellipsoids are given at 50% probability.

Ring closures of this type have been reported before. Ovalle et al. reported on the attempted synthesis of L^4 using a synthesis similar to the one reported here [25]. In their study they attempted to purify the polydentate amine using column chromatography (silica). However instead of isolating L^4 they obtained the corresponding tris-indazole in good yield. The mechanism of ring closure in this instance has not been rigorously investigated. Previous reports on tetradentate N_4 secondary amine and Schiff base complexes has shown a tendency for the anilino group to deprotonate in the presence of metals to form a coordinated amide [26]. We were hoping to use chemistry of this nature to ultimately activate the aniline and coax the polydentate ligand to bridge and form multimetallic complexes. Instead the deprotonation of the aniline in close proximity to the coordinated secondary amine would seem to initiates ring closure within the crowded coordination sphere. The ease with which this ring closure reaction takes place goes some way to explain why the synthetic protocol (direct precipitation; no heating) employed here for the isolation of the primary complexes was found to be the most suitable. It also goes some way to explain the discrepancy in the mass spectra of the nickel complexes compared with the corresponding copper complexes. The nickel complex, by virtue of its better stability gives rise to a parent peak at m/e 518. In

contrast the copper complex gives rise to a plethora of signals between m/e 512 (tris-indzole) and 520. The latter is consistent with the sequential loss of H_2 during ligand rearrangement.

Concluding remarks

Our studies on heptadentate ligands (N_4O_3, N_4S_3, N_4N_3) is complete with this partially successful report on the synthesis on potentially heptadentate ligands. The general absence of tren based polyamine systems in the literature has always presented itself as a curious omission especially as the tetradentate systems have been know for many years and that studies on high dentictity salicylaldehyde species were also reported over 60 years ago [1, 27]. The study here finally shows that it is possible to generate these species. While their primary coordination chemistry is in line with previous studies regrettably their stability is poor. The placement of an amine adjacent to a Schiff base linkage was, in retrospect, expected to give rise to intra-molecular chemistry. However reduction of the Schiff base linkage normally give rise to more robust species and what was not anticipated was that in contrast to the salicylaldehyde motif that the aniline based species were not completely passivated by the formation of secondary amines.

Footnotes

* There is evidence that this material is ultimately a yellow solid.

Supporting information

Details of the X-ray crystal structure determinations may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www:http://ccdc.cam.ac.uk) on request quoting the depository numbers CCDC 1535536-1535541

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