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

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### ABSTRACT

The synthetic utility of tris-((2-hydroxybenzyl)-aminoethyl)amine (H6TrenSal) and tris-((2-hydroxy-5-bromobenzyl)-aminoethyl)amine (H6Tren5BrSal) are investigated. A range of monomeric complexes with general formula [(H6TrenSal)M][NO<sub>3</sub>] with nickel, copper and zinc are reported and crystallographically analysed. Nickel adopts three motifs which are different to that observed for copper and zinc. The use of these species as platforms for the synthesis of more complex systems in conjunction with the lanthanoids are explored. Copper and zinc do not follow a similar reaction pathway to nickel. While nickel forms the expected trimetallic motif [{(TrenSal)Ni}<sub>2</sub>Ln(HOMe)]<sup>+</sup>, copper forms a copper trimetallic motif. In contrast to both nickel and copper, reactions with [(H6TrenSal)Zn]<sup>+</sup> produce lanthanoid based products namely [(H6Tren5BrSal)Gd(NO<sub>3</sub>)<sub>3</sub>] and [{(H6TrenSal)Ce}<sub>2</sub>- $\mu^2$ -O<sub>2</sub>].

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#### 1. Introduction

Multidentate ligands such as EDTA, DTPA and TrenSal, with six or more donor atoms are generally designed to encapsulate metal cations [1-6]. In this respect the TrenSal motif (Fig. 1) has come to our attention because its structure contains flexible and inflexible regions, and it has the ability to change denticity [6,7]. TrenSal is potentially trianionic and it is thus, unsurprising that it forms discrete hexadentate complexes with trivalent metals [4,5]. However, with divalent metals [6,7] more complex multi-metallic complexes are formed in order to balance the charge and satisfy the preferred coordination geometry of the metal centres (Fig. 1). Thus with nickel trimetallic complexes where each nickel sits in an octahedral environment are retrieved [6], whereas with copper the ligand moves to a heptadentate mode and the complex is found to be tetrametallic [7]. This change is believed to be driven by the articulation in the apical region of the ligand (centred on N2, Fig. 1). Intriguingly, hydrogenating the imine thus forming the secondary amine, H6TrenSal, can increase the flexibility around the aminoethyl region of the ligand further.

A number of complexes employing H6TrenSal have been reported previously [8–11]. These broadly fall into two categories: simple mono-metallic species [8-10] and more complex trimetallic complexes [11]. Mono-metallic compounds form with trivalent metals (e.g. gallium, indium). In these instances the metals sit within an N<sub>y</sub>O<sub>x</sub> (where y = 3, x = 3; y = 4, x = 2, 3) motif preferring to complex with the ligands apical nitrogen rather than the phenoxide donors (Fig. 1) [8]. This is in contrast to the respective Tren-Sal complexes where the encapsulated metal is held in a symmetric N<sub>3</sub>O<sub>3</sub> environment which employs all three phenoxide donors [6,12]. Thus it would seem that the flexibility of the H6TrenSal can allow the complexing metals to position themselves within the pocket formed by the folded ligand. Trimetallic complexes (typically  $[{(H6TrenSal)Ni}_2Ln(OMe)]^+$ : Ln = lanthanoid) arise from the putative residual charge on the primary [(H6Tren-Sal)Ni]<sup>+</sup> complex and the manner in which the compensating lanthanide cation binds to and assembles the two sets of phenoxide donors [11]. In this way the ligand forms a cage around the nickel cations with the transition metal sitting within an N<sub>4</sub>O<sub>2</sub> motif. This motif is less common for Schiff base species but two similar complexes, viz. [{(TEtSal)Ni}<sub>2</sub>Pb] and [{(TMeSal)Ni}<sub>2</sub>Gd]<sup>+</sup>, have recently been reported [6,12].

We are studying the manner in which ligands support the formation of multi-metallic complexes [13–15]. Our current synthetic design [6] has been based on the use of multidentate, salicylidene, Schiff base ligands such as TrenSal. In view of the greater flexibility





Abbreviations: EDTA, ethylenediaminetetraacetic acid; DTPA, diethylenetriaminepentaacteic acid; TrenSal, tris-((2-hydroxybenzylidene)-aminoethyl)amine; Tren5BrSal, tris-((2-hydroxy-5-bromobenzylidene)-aminoethyl)amine; H6TrenSal, tris-((2-hydroxybenzyl)-aminoethyl)amine; H6Tren5BrSal, tris-((2-hydroxy-5-bromobenzyl)-aminoethyl)amine.

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Fig. 1. The chemical structure of TrenSal (left) and the X-ray crystal structures of [(Tren5BrSal)<sub>2</sub>Ni<sub>3</sub>] (middle) [6] and [(Tren5BrSal)<sub>2</sub>Cu<sub>4</sub>O] (right) [7].

of the respective hydrogenated species, we have extended our interest to H6TrenSal. Although our interests are primarily based on the use of first row transition metals, the studies of Orvig et al. [11] suggest that it should be able to encapsulate first row metals using the lanthanides. This suggested that we should initially focus on the simple adducts of nickel, copper and zinc with H6TrenSal and their subsequent combination with lanthanides.

### 2. Experimental

All experiments were carried out using standard apparatus and commercially available chemicals. TrenSal was prepared as previously reported [6]. NMR analysis was carried out on a Bruker AMX 400 operating at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C. 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. Infra red spectra were recorded as potassium bromide discs using a Nicolet Avatar 360 FTIR spectrometer. Magnetic measurements were determined at room temperature in the solid state using an MSB1 magnetic susceptibility balance. All X-ray measurements were conducted using a Nonius Kappa CCD diffractometer at 123 K using graphite monochromated Mo Kα radiation apart from [(H6Tren5BrSal)Ni], data for which was collected on a Oxford Diffraction Xcalibur CCD diffractometer.

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  $F^2$ , 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 and SHELXS-97 [16] and the graphical interface WinGX [17]. A summary of the crystallographic parameters is given in Table 1.

### 2.1. Hydrogenation of TrenSal and Tren5BrSal to give H6TrenSal and H6Tren5BrSal

Sodium borohydride (3–4 mol equiv.) was added in small portions over a period of 1 h to a solution of the relevant Schiff base (TrenSal, Tren5BrSal; 1 mol equiv.) in methanol under a blanket of nitrogen. The yellow solution became colourless. The mixture was stirred overnight to ensure the reaction was complete. The solvent was removed by rotary evaporation and 6 g of ammonium acetate in 100 ml distilled water was added. The product was then extracted into  $3 \times 100$  ml chloroform. The extracts were combined, washed with 100 ml of distilled water and dried over anhydrous sodium sulphate. The solution was filtered and the solvent removed to give the desired product. Typical yields of 60–80% were obtained.

### 2.1.1. H6TrenSal

It was obtained as a viscous oil which was used without further purification.  $\delta_{\rm H}$  (400 MHz; solvent CDCl<sub>3</sub>) 7.15 (t, 3H, arom), 7.00 (d, 3H, arom), 6.80 (m, 6H, arom), 4.00 (s, 6H, -Ph- $CH_2$ -NH-), 2.70 (t, 6H, -NH<sub>2</sub>- $CH_2$ - $CH_2$ -N-), 2.60 (t, 6H, -NH<sub>2</sub>- $CH_2$ - $CH_2$ -N-), 2.60 (t, 6H, -NH<sub>2</sub>- $CH_2$ - $CH_2$ -N-).  $\delta_{\rm C}$  (100 MHz; solvent CDCl<sub>3</sub>) 160, 129, 128, 122, 119, 116 (arom), 55 (-Ph- $CH_2$ -NH-), 52 (-NH<sub>2</sub>- $CH_2$ -CH<sub>2</sub>-N-), 46 (-NH<sub>2</sub>- $CH_2$ -CH<sub>2</sub>-N-). Mass Spec. (ESI) m/z 465 [M-H<sup>+</sup>].

#### 2.1.2. H6Tren5BrSal

It was obtained as a solid which was recrystallised from dichloromethane/methanol by vapour diffusion. Crystal suitable for structural analysis were obtained from this process. Found: C, 45.77; H, 5.40; N, 7.43%. Expected for C<sub>27</sub>H<sub>33</sub>N<sub>4</sub>Br<sub>3</sub>O<sub>3</sub> · MeOH: C, 45.86; H, 5.09; N, 7.64.  $\delta_{\rm H}$  (400 MHz; solvent CDCl<sub>3</sub>) 7.22 (dd, 3H, arom,  $J_1$  = 2.3 Hz,  $J_2$  = 8.6 Hz), 7.05 (d, 3H, arom,  $J_1$  = 2.3 Hz), 6.55 (d, 3H, arom,  $J_2$  = 8.6 Hz), 3.9 (s, 6H, -Ph-CH<sub>2</sub>-NH-), 3.5 (s, 3H, -NH-), 2.70 (t, 6H, -N-CH<sub>2</sub>-CH<sub>2</sub>-NH-), 2.5 (t, 6H, -N-CH<sub>2</sub>-CH<sub>2</sub>-NH-).  $\delta_{\rm C}$  (100 MHz; solvent CDCl<sub>3</sub>) 157, 131, 130, 124, 118, 111 (arom), 54 (-Ph-CH<sub>2</sub>-NH-), 52 (-N-CH<sub>2</sub>-CH<sub>2</sub>-NH-), 46 (-N-CH<sub>2</sub>-CH<sub>2</sub>-NH-). FTIR [ $\nu$ /cm<sup>-1</sup> (KBr)]: 3450 (OH br), 1470 (C=C), 1100, 1025, 1265 (C-O), 820 (arom). Mass Spec (ESI) *m/z* 699, 701, 703, 705 (1:3:3:1) [M-H<sup>+</sup>], m.p. 68 °C.

## 2.2. Preparation of [Ni(H6TrenSal)(OH<sub>2</sub>)][NO<sub>3</sub>], [Ni(H6TrenSal)][NO<sub>3</sub>] and [Ni(H6Tren5BrSal)(OH<sub>2</sub>)][NO<sub>3</sub>]

A methanolic solution of nickel nitrate (1.1 g, 3.8 mmol) was added to a solution containing the relevant Schiff base (1.8 g and 2.7 g respectively, 3.9 mmol) dissolved in methanol (50 ml). The mixture was stirred for 1 h at 50 °C whereupon the resultant purple solution was allowed to cool and the solvent removed under reduced pressure. The sticky purple material was washed with dichloromethane, water and diethyl-ether to obtain a pale purple powder. Yields are typically 60–70%.

X-ray quality crystals of  $[Ni(H6TrenSal)(OH_2)][NO_3]$  were grown by slow evaporation of the product from ethanol on the open bench.

[Ni(H6TrenSal)(OH<sub>2</sub>)][NO<sub>3</sub>]: Anal. Calc. for C<sub>27</sub>H<sub>37</sub>N<sub>5</sub>Ni<sub>1</sub>O<sub>7</sub>: C, 53.84; H, 6.19; N, 11.63. Found: C, 54.07; H, 6.43; N, 11.48%. FTIR

Table 1	l
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Crystallographic parameters

	H6Tren5BrSal CH₃OH	H6TrenSal (NO <sub>3</sub> ) <sub>3</sub>	[(H6TrenSal)Ni] NO <sub>3</sub> · CH <sub>3</sub> OH	[(H6TrenSal)Ni(OH <sub>2</sub> )] NO <sub>3</sub> · CH <sub>3</sub> OH	[(H6Tren5BrSal)Ni] · 2CH <sub>3</sub> OH	[(H6TrenSal)Cu] NO <sub>3</sub> · 0.7MeOH	[(H6TrenSal)Zn] NO <sub>3</sub> · 1H <sub>2</sub> O	[(H6Tren5Br)Zn] NO <sub>3</sub> · Et <sub>2</sub> O	[{(H6TrenSal}Ni) <sub>2</sub> - La (HOMe)] NO <sub>3</sub>	[{(H6TrenSal}Ni) <sub>2</sub> - Ce (H <sub>2</sub> O)] K <sub>0.5</sub> (NO <sub>3</sub> ) <sub>2.5</sub>	[(H6TrenSal)Gd(NO <sub>3</sub> ) <sub>3</sub> ] CH <sub>2</sub> Cl <sub>2</sub> · CH <sub>3</sub> OH	[(H6TrenSal)Ce] <sub>2</sub> O <sub>2</sub> 2DMF 2Et <sub>2</sub> O
Empirical formula	C <sub>28</sub> H <sub>37</sub> Br <sub>3</sub> N <sub>4</sub> O <sub>4</sub>	$C_{27}H_{39}N_7O_{12}$	$C_{28}H_{39}N_5NiO_7$	$\mathrm{C}_{29}\mathrm{H}_{43}\mathrm{N}_{5}\mathrm{NiO}_{8}$	$C_{29}H_{39}Br_3N_4NiO_5$	$C_{27.7}H_{37.8}N_5O_{6.7}$	$C_{27}H_{37}N_5O_7Zn_1$	$C_{31}H_{42}Br_3N_5O_7Zn$	C <sub>57.50</sub> H <sub>80.50</sub> La- N <sub>9</sub> N <sub>i2</sub> O <sub>16</sub>	C <sub>54</sub> H <sub>70</sub> CeK <sub>0.50</sub> - N <sub>10.50</sub> Ni <sub>2</sub> O <sub>15.5</sub>	$C_{29}H_{39}Br_3Cl_2Gd_1N_7O_{13}\\$	$C_{68}H_{100}Ce_2N_{10}O_{12}$
FW	733.35	653.65	616.35	648.943	822.08	611.56	608.99	901.80	1410.14	1391.42	1161.55	1529.82
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	orthorhombic	orthorhombic	triclinic
Space group	$P2_1/n$	P212121	Pbca	C2/c	$P2_1/n$	C2/c	C2/c	Pbca	ΡĪ	Fddd	Pbca	PĪ
a (Å) b (K) c (K) $\alpha (°)$ $\beta (°)$	9.5986(3) 14.5471(4) 21.6731(7) 97.718(2)	9.6620(2) 12.8230(4) 24.4840(8)	15.0819(2) 19.5887(3) 19.6601(3)	25.6110(8) 14.8150(5) 16.5470(4)	13.9434(4) 17.5746(5) 13.9593(4))	26.2890(12) 13.3002(6) 17.1790(6)	26.2391(9) 13.4200(4) 17.1144(5)	12.9220(6)_ 17.4571(7) 31.4840(16)	13.0710(3) 14.1409(4) 19.8191(5) 74.535(2) 84.324(2)	17.3039(6) 37.3922(7) 42.9281(14)	15.2796(3) 21.4716(4) 23.8526(5)	10.8974(8) 12.9973(10) 13.7157(11) 88.237(3) 77.694(5)
γ(°)	57.710(2)		_	55.502(2)		55.715(2)	55.507(2)		67.067(2)			65.256(5)
Z	4	4	8	8	4	8	8	8	2	16	8	2
$V(A^3)$ $\mu_{calc}$ $(mm^{-1})$	2998.84(16) 4.075	3033.47(15) 0.114	5808.28(15) 0.722	6268.0(3) 0.675	3190.38(16) 4.409	5976.8(4) 0.781	5998.7(3) 0.869	7102.2(6) 4.119	3251.53(14) 1.288	27775.8(14) 1.276	7825.5(3) 4.965	1720.0(2) 1.374
Number of reflections measured	44168	25317	85884	36666	14745	11484	42845	29830	74773	33014	65 1 40	30802
Number of unique reflections	6901	5360	6319	7181	6006	5888	6606	6223	12789	6143	7691	6657
Number observed	4958	3975	4967	4961	4328	3393	4066	4061	7758	5023	5224	4333
T <sub>min</sub>	0.544	na	0.911	na	0.375	na	na	0.730	na	na	0.6655	0.552
T <sub>max</sub>	1.000	na	1.000	na	1.000	na	na	1.000	na	na	1.0000	0.745
R <sub>int</sub>	0.0665	0.063	0.0791	0.057	0.0402	0.0981	0.071	0.1393	0.1437	0.0408	0.0815	0.1646
Number of parameters	381	414	389	415	383	390	387	428	822	385	522	423
$R(I > 2\sigma(I))$	0.0451	0.048	0.0630	0.0483	0.0499	0.0655	0.0534	0.0922	0.0614	0.0501	0.0416	0.0675
R <sub>w</sub> (all reflections)	0.1087	0.0967	0.1157	0.1217	0.1223	0.1594	0.1651	0.2115	0.1483	0.1554	0.0900	0.1686
Goodness- of-fit	1.0541	1.044	1.160	1.023	0.996	1.037	1.049	1.083	1.053	1.083	1.010	1.032

 $[(\nu/cm^{-1} (KBr)]: 3440 (br OH); 2930 (weak NH); 1480 (C=C); 1300 (C-O); 755 (arom). Mass spec. (ESI) m/z 521 (70%, LNi<sup>+</sup>), 465 (100% LH<sup>+</sup>). <math>\lambda_{max}$  (solid reflectance) 571 nm.

X-ray quality crystals grown from methanol/diethyl-ether by vapour diffusion were revealed to be the unhydrated product.

[Ni(H6TrenSal)][NO<sub>3</sub>] · MeOH: Anal. Calc. for  $C_{28}H_{39}N_5Ni_1O_7$ : C, 54.57; H, 6.38; N, 11.36. Found: C, 54.47; H, 6.18; N, 11.47%. FTIR [( $\nu$ /cm<sup>-1</sup> (KBr)]: 3440 (br OH); 2930 (weak NH); 1480 (C=C); 1300 (C−O); 755 (arom). Mass spec. (ESI) m/z 521 (70%, LNi<sup>+</sup>), 465 (100% LH<sup>+</sup>).  $\lambda_{max}$  (solid reflectance) 581 nm.

X-ray quality crystals grown from methanol/diethyl-ether by vapour diffusion were revealed to be a neutral product.

[Ni(H6Tren5BrSal)] · MeOH: Anal. Calc. for  $C_{27}H_{31}Br_3N_4Ni_1O_3$ : C, 42.62; H, 4.47; N, 7.10. Found: C, 42.20; H, 3.56; N, 7.65%. FTIR [( $\nu/cm^{-1}$  (KBr)]: 3425 (br OH); 2930 (weak NH); 1480 (C=C); 1300 (C-O); 755 (arom). Mass spec. (ESI) m/z 759 (100% LNiH<sup>+</sup>).  $\lambda_{max}$  (solid reflectance) 590 nm.

## 2.3. Preparation of $[Cu(H6TrenSal)][NO_3]$ and $[Cu(H6Tren5BrSal)][NO_3]$

A methanolic solution (15 ml) of copper nitrate dihydrate (0.4 g, 0.86 mmol) was added to a solution containing the relevant Schiff base (0.4 g and 0.6 g respectively, 0.86 mmol) dissolved in methanol (20 ml). Three drops of triethylamine were added and the green solution stirred for 20 min at 50 °C. The solution was allowed to cool and then filtered. On prolonged standing (24 h) the product crystallises from solution. Yield 67%.

[Cu(H6TrenSal)][NO<sub>3</sub>]: Anal. Calc. for  $C_{27}H_{35}N_5Cu_1O_6 \cdot 2H_2O$ : C, 51.87; H, 6.29; N, 11.59. Found: C, 51.79; H, 6.77; N, 11.59%. FTIR [( $\nu$ /cm<sup>-1</sup> (KBr)]: 3410 (br OH); 2925 (weak NH); 1480 (C=C); 1385 (NO<sub>3</sub>); 1280 (C–O); 770 (arom). Mass spec. (ESI) m/z 526 (100%, LCu<sup>+</sup>).  $\lambda_{max}$  (solid reflectance) 675 nm.

Crystals of [Cu(H6Tren5BrSal)][NO<sub>3</sub>] were grown from methanol/diethyl-ether by vapour diffusion. Although these were subjected to analysis by X-ray methods the data did not refine to an acceptable degree. Thus only the identity of the compound and the connectivity of the atoms can be confirmed. The data was not deposited with the CCDC but can be found in the Supplementary material.

[Cu(H6Tren5BrSal)][NO<sub>3</sub>]: FTIR [( $\nu$ /cm<sup>-1</sup> (KBr)]: 3410 (br OH); 2935 (weak NH); 1470 (C=C); 1385 (NO<sub>3</sub>); 1270 (C–O); 820 (arom). Mass spec. (ESI) *m*/*z* 764 (100%, LCu<sup>+</sup>).  $\lambda$ <sub>max</sub> (solid reflectance) 681 nm, 813 nm.

# 2.4. Preparation of [Zn(H6TrenSal)][NO<sub>3</sub>] and [Zn(H6Tren5BrSal)][NO<sub>3</sub>]

A methanolic solution (10 ml) of zinc nitrate hexahydrate (0.05 g, 0.25 mmol) was added to a solution containing the relevant Schiff base (0.12 g and 0.17 g respectively, 0.25 mmol) dissolved in methanol (10 ml). The colourless solution was stirred for 20 min at 50 °C. The solution was allowed to cool and then filtered. On prolonged standing (24 h) the product crystallises from solution. Yield 71%.

$$\label{eq:constraint} \begin{split} &[\text{Zn}(\text{H6TrenSal})][\text{NO}_3]: \textit{Anal. Calc. for $C_{27}H_{35}N_5Zn_1O_6 \cdot 2H_2O$: C,} \\ &51.72; \textit{H, 6.27; N, 11.17. Found: C, 51.79; H, 6.23; N, 11.20\%. FTIR} \\ &[(\nu/cm^{-1}~(KBr)]: 3460~(br~OH); 2940~(weak~NH); 1455~(C=C); 1385~(NO_3); 1280~(C-O); 755~(arom). Mass spec. (ESI) $m/z$ 527~(100\%, LZn^+). \end{split}$$

Crystals of [Zn(H6Tren5BrSal)][NO<sub>3</sub>] suitable for X-ray analysis were grown from methanol/diethyl-ether by vapour diffusion.

 $[Zn(H6Tren5BrSal)][NO_3] \cdot (C_2H_5)_2O:$  Anal. Calc. for  $C_{31}H_{42}Br_3N_5$ -Zn<sub>1</sub>O<sub>7</sub>: C, 41.28; H, 4.69; N, 7.77. Found: C, 41.63; H, 4.70; N, 7.98%. FTIR  $[(v/cm^{-1} (KBr)]:$  3420 (br OH); 2920 (weak NH); 1475 (C=C); 1390 (NO<sub>3</sub>); 1275 (C-O); 815 (arom). Mass spec. (ESI) m/z 765 (100%, LZn<sup>+</sup>).

### 2.5. Preparation of Di-(tris-(2-hydroxybenzyl)aminoethylamine nickel-methanolo-lanthanum nitrate

[Ni(H6TrenSal)(OH<sub>2</sub>)][NO<sub>3</sub>] (0.1 g, 0.17 mmol) was dissolved in 15 ml methanol to which five drops of triethylamine were added. The solution was stirred at 60 °C for 5 min whereupon a methanolic solution of lanthanum nitrate hexahydrate (0.04 g, 0.09 mmol) was added dropwise. The resulting solution was stirred for 15 min, allowed to cool and then filtered. The product forms as light purple powder crystals that were suitable for analysis by X-ray methods. Yield 59%. Anal. Calc. for  $C_{54}H_{78}La_1N_8Ni_2O_{12}$ : C, 47.81; H, 5.93; N, 9.12. Found: C, 47.70; H, 5.93; N, 8.92%. FTIR [( $\nu/$  cm<sup>-1</sup> (KBr)]: 3430 (br OH); 2850 (weak NH); 1595 (NO<sub>3</sub>), 1485 (C=C); 1295 (C–O); 760 (arom). Mass spec. (ESI) m/z 1173 (10%, (LNi)<sub>2</sub>La<sup>+</sup>), 526 (100%, LNi<sup>+</sup>).  $\lambda_{max}$  (solid reflectance) 550 nm, 920 nm.

### 2.6. Preparation of di-(tris-(2-hydroxybenzyl)aminoethylamine nickel) cerium nitrate

[Ni(H6TrenSal)(OH<sub>2</sub>)][NO<sub>3</sub>] (0.2 g, 0.33 mmol) was dissolved in methanol (20 ml) to which five drops of triethylamine was added. The solution was stirred for 10 min at 60 °C, whereupon a methanolic solution of cerium(III) nitrate hexahydrate (0.072 g, 0.11 mmol) was added dropwise. The solution turned deep orange. After stirring for further 15 min, the solution was filtered and allowed to cool. The product forms as an orange powder. Yield 68%. Crystals suitable for analysis by X-ray crystallography were obtained by slow evaporation of orange filtrate. FTIR [( $\nu$ /cm<sup>-1</sup> (KBr)]: 3440 (br OH); 2870 (weak NH); 1485 (C=C); 1390 (NO<sub>3</sub>), 1250 (C–O); 760 (arom). Mass spec. (ESI) *m*/*z* 1179 (100%, (LNi)<sub>2</sub>Ce<sup>+</sup>). During optimisation of the mass spectral analysis the dication *m*/*z* 589 ((LNi)<sub>2</sub>Ce<sup>2+</sup>) can be a prominent feature.  $\lambda_{max}$  (solid reflectance) 540 nm.

### 2.7. Preparation of di-(tris-(2-hydroxybenzyl)aminoethylamine copper) copper tetranitrate

[(H6TrenSal)Cu][NO<sub>3</sub>] (0.4 g, 0.86 mmol) was dissolved in 15 ml methanol to which five drops of triethylamine were added. The solution was stirred at 60 °C for 5 min whereupon a methanolic solution of lanthanum nitrate hexahydrate (0.185 g, 0.43 mmol) was added dropwise. The resulting solution was stirred for 15 min, allowed to cool and then filtered. The product forms as brown/purple powder crystals that were subjected to analysis by X-ray methods. Yield 51%. Anal. Calc. for  $C_{54}H_{70}Cu_3N_{12}O_{18} \cdot 4H_2O$ : C, 44.78; H, 5.23; N, 11.19. Found: C, 44.25; H, 4.92; N, 11.46%. FTIR [( $\nu$ /cm<sup>-1</sup> (KBr)]: 3440 (br OH); 2930 (weak NH), 1485 (C=C); 1385 (NO<sub>3</sub>); 1260 (C–O); 755 (arom). Mass spec. (ESI) m/z 1116 (100%, ( $L_2Cu_3^+$ ) 526 ( $LCu^+$ ).  $\lambda_{max}$  (solid reflectance) 409 nm, 646 nm.

Although the sample was subjected to analysis by X-ray methods the data did not refine to an acceptable degree. Thus only the identity of the compound and the connectivity of the atoms can be confirmed. The data was not deposited with the CCDC but can be found in the Supplementary material.

#### 2.8. Preparation of [(H6Tren5BrSal)Gd(NO<sub>3</sub>)<sub>3</sub>]

[(H6TrenSal)Zn][NO<sub>3</sub>] (0.5 g, 0.86 mmol) was dissolved in 10 ml methanol to which five drops of triethylamine were added. The solution was stirred at 90 °C for 10 min whereupon a methanolic solution of gadolinium nitrate hexahydrate (0.024 g, 0.05 mmol) was added dropwise. The resulting solution was stirred for 15 min, allowed to cool and then filtered. The product forms as white powder. Crystals suitable for X-ray analysis were obtained by vapour diffusion of the mother liquors with diethyl-ether. Yield

46%. FTIR [(v/cm<sup>-1</sup> (KBr)]: 3430 (br OH); 2940 (weak NH), 1470 (C=C); 1385 (NO<sub>3</sub>); 1260 (C–O); 755 (arom).

### 2.9. Preparation of [{(H6TrenSal)Ce}<sub>2</sub>- $\mu^2$ -O<sub>2</sub>]

[(H6TrenSal)Zn][NO<sub>3</sub>] (0.5 g, 0.86 mmol) was dissolved in 10 ml methanol. The solution was stirred at 90 °C and treated with three drops of a methanolic solution of KOH followed by cerium nitrate hexahydrate (0.2 g 0.5 mmol) in methanol (10 ml). The resulting solution was stirred for 15 min, allowed to cool whereupon orange crystals form. Crystals that were suitable for analysis by X-ray methods were grown from DMF/diethyl-ether by vapour diffusion. Yield 45%. Anal. Calc. for  $C_{54}H_{66}Ce_2N_8O_8$ : C, 53.95; H, 5.53; N, 9.32. Found: C, 53.85; H, 6.60; N, 8.77%. FTIR [( $\nu/cm^{-1}$  (KBr)]: 3405 (br OH); 2900 (weak NH), 1480 (C=C); 1290 (C–O); 765 (arom). Mass spec. (ESI) m/z (100%, (LCe<sup>+</sup>) 601.  $\lambda_{max}$  (solid reflectance) 431 nm.  $\mu_{eff}$  1.3 BM.

#### 3. Results and discussion

The multidentate ligand systems H6TrenSal and H6Tren5BrSal can be prepared with ease by hydrogenating the Schiff base species generated from the tris-(2-aminoethyl)amine and salicylaldehyde (H6TrenSal) or 5-bromosalicylaldehyde (H6Tren5BrSal). X-ray quality crystals of H6Tren5BrSal can be easily grown from dichloromethane (Fig. 2). In contrast H6TrenSal is received as an oily material that is used without further purification. However, a small number of X-ray quality crystals we generated as a bi-product of the reactions of the nitrate salts discussed below. Taken together these structures elegantly demonstrate the flexibility of these multidentate species. The neutral species forms a zwitterion that is heavily folded due to hydrogen bonding interactions, whereas the nitrate salt being devoid of a hydrogen bonded network adopts a more open dendritic form.

Although a number of mono-metallic complexes employing this ligand type have been reported previously [8], curiously no simple examples of transition metal complexes have been structurally characterised. Thus treatment of the two hydrogenated Schiff bases, H6TrenSal and H6Tren5BrSal, with one equivalent of metal nitrate (M = Ni, Cu, Zn) leads to the formation of cationic 1:1 adducts. Although the metal ligand ratios are the same throughout four distinct structural types are retrieved: a dominant five coordinate N<sub>4</sub>O motif (Fig. 3a, e.g. copper), and three six coordinate mo-

tifs one where the coordination sphere is completed with water (Fig. 3b), another where a second phenol donor (i.e.  $N_4O_2$ ) is employed which is cationic (Fig. 3c) and a third species ([(H6Tren5-BrSal)Ni] Fig. 3d which also employs two phenolates but which is now neutral.

As predicted the flexibility of the hydrogenated ligand allows the metals to sit within the pocket defined by the four nitrogen donors (the N2-M-N angles are all less than 90°, Table 2) and all the species share the common MN<sub>4</sub> motif. Indeed the metrical parameters of the MN<sub>4</sub> motif for all the compounds isolated are remarkably similar (Table 2). Copper and zinc complete their coordination sphere by binding to a single phenoxide. In contrast nickel was isolated in two hexadentate forms, one which is effectively the copper/zinc structure with an additional coordinated water molecule, an "anhydrous" form where a second phenoxide rotates into the sixth coordination site and a neutral species where the phenolate has been deprotonated. The two five coordinate complexes (Cu, Zn) are trigonal bipyramidal in nature with a phenoxide donor filling the fifth position trans to the apical nitrogen (N2, Table 2). The ambivalent coordination chemistry of TrenSal has been remarked upon previously by Lui et al. [8] in their reports on their group 13 complexes. Here three distinct structural types are reported; an N<sub>3</sub>O<sub>3</sub> coordination mode with aluminium, an N<sub>4</sub>O motif with gallium and an N<sub>4</sub>O<sub>3</sub> motif with indium. The structures reported here for copper and zinc follow that of the adjacent element gallium (Table 2) in that they also display two pendant phenoxides. The two structures isolated which contain nickel (viz. the N<sub>4</sub>O and N<sub>4</sub>O<sub>2</sub> motifs) are further additions to the H6Tren-Sal family of complexes. These two structural motifs can be considered to lie intermediate between the N<sub>4</sub>O structure of gallium and N<sub>4</sub>O<sub>3</sub> indium [8] and can thus be considered to be part of a wider structural progression.

Bayly et al. have reported the synthesis of an interesting series of nickel lanthanoid trimetallic species [11]. The synthetic protocols employed in his study were simple and relied on the selfassembly of the complex from a mixture of the three components (two metal salts and the ligand). A mechanism for the assembly of these species can be drawn up which employs the pre-formation of a moiety such as those described above (Fig. 3). This hypothesis was tested by treating [(H6TrenSal)Ni]<sup>+</sup> with lanthanum and cerium(III) nitrate. Not only did the spectroscopic data agree with that previously published by Bayly et al. [11] for [(NiTren-Sal)<sub>2</sub>La(OMe)]NO<sub>3</sub>, consistent with his claims regarding the pro-



**Fig. 2.** The X-ray crystal structure of H6Tren5BrSal (left) and [H6TrenSal][NO<sub>3</sub>]<sub>3</sub> (right nitrates not shown). The entrapped methanol (C28, O4) in the structure of H6Tren5BrSal can be seen. The molecule folds due to intramolecular hydrogen bonding (dotted lines) between O1 and H31 (1.626 Å) and O1 and H1 (1.820 Å). The hydrogen from O1 has effectively migrated to N3. The crystals of [H6TrenSal][NO<sub>3</sub>]<sub>3</sub> (right) were obtained as a minor bi-product of the metal nitrate reactions and is included here to demonstrate the structural extremes available to these ligand systems. Thermal ellipsoids are at 50% probability.



**Fig. 3.** The X-ray crystal structures of [(H6TrenSal)Cu]<sup>+</sup> (top), [(H6TrenSal)(H<sub>2</sub>O)Ni]<sup>+</sup> (middle left), [(H6TrenSal)Ni]<sup>+</sup> (middle right) and [(H6Tren5BrSal)Ni] (bottom). The structure of [(H6TrenSal)Zn]<sup>+</sup>, [(H6Tren5BrSal)Cu]<sup>+</sup> and [(H6Tren5BrSal)Zn]<sup>+</sup> (not shown) are isostructural with that of [(H6TrenSal)Cu]<sup>+</sup>. For clarity the nitrate counterions are not shown. Thermal ellipsoids are shown at 50% probability.

pensity of these species to crystallise we were able to retrieve Xray quality crystals directly from the reaction mixture for these two complexes (Fig. 4). Thus the mechanism for the synthesis of these species can now be further refined. The lanthanoid initially chelates to the two coordinated phenoxides (O1, O2, Fig. 4 bottom). Since the nickel sits within the N4 pocket it is difficult for the third phenoxide to coordinate to the internalised metal. However, the chelated lanthanoid adopts a more appropriate position where

 Table 2

 The metrical parameters of the H6TrenSal and H6Tren5BrSal complexes of nickel, copper, zinc and gallium

	-			
	M-N <sub>apex</sub> (Å)	M–N (Å)	$\angle N-M-N_{apex}$ (°)	$\angle O_{phenox}-M-N_{apex}$ (°)
[(H6TrenSal)(H <sub>2</sub> O)Ni] <sup>+</sup>	2.088	2.120, 2.057, 2.189	83.80, 85.36, 81.66	177.43
[(H6TrenSal)Ni] <sup>+</sup>	2.102	2.128, 2.138, 2.062	84.16, 82.68, 83.93	175.11
[(H6Tren5BrSal)Ni]	2.127	2.119, 2.150, 2.169	81.33, 84.00, 81.04	170.12
[(H6TrenSal)Cu] <sup>+</sup>	2.034	2.050, 2.127, 2.120	85.47, 85.61, 84.22	175.84
[(H6TrenSal)Zn] <sup>+</sup>	2.200	2.112, 2.062, 2.098	81.39, 84.27, 82.33	170.97
[(H6Tren5BrSal)Zn] <sup>+</sup>	2.216	2.054, 2.101, 2.112	82.1, 82.7, 84.2,	171.3
[(H6Tren5BrSal)Ga] <sup>+</sup>	2.147	2.090, 2.099, 2.115	81.7, 82.8, 80.9	172.7



**Fig. 4.** The X-ray crystal structure of  $[(H6TrenSalNi)_2La(OMe)]^+$ . The complex is isostructural with the nickel lanthanoid complexes reported by Bayly et al. [11]. The thermal ellipsoids are shown at 50% probability.

the pendant phenoxide is able to bind independently to lanthanoid centre. Thus in contrast to the Schiff base species the binding of the heavy metal is not symmetric.

Our ability to generate the simple compounds of copper and zinc similar to nickel (Fig. 2) suggested that the reaction reported by Bayly et al. [11] might also give rise to an interesting series of lanthanoid complex of these metals. Unfortunately the reaction failed to generate the desired isostructural species presumably because, unlike nickel, the phenoxides do not form a chelating cleft (Fig. 2). From the reaction of [(TrenSal)Cu]<sup>+</sup> with lanthanum nitrate we obtained a homotrimetallic  $(M_3L_2)$  copper complex (Fig. 5) where three coppers are found to sit in two unique environments. The central copper (Cu2) is chelated between two [(TrenSal)Cu] species and sits in an essentially planar environment. The coppers encapsulated by TrenSal remain five coordinate employing an N<sub>3</sub>O<sub>2</sub> donor set. The distance to the apex nitrogen is now somewhat larger ( $\sim$ 2.37 Å, cf. Table 2) indicative that the encapsulated copper (Cu1) is being pulled forward due to the presence of the central metal (Cu2). A pendant phenolic group is still present except that it now includes its attendant secondary amine which is protonated. As an O<sub>3</sub> octahedral motif is not demanded by the central copper (cf. Ln, Ni) there is no driving force for the separation of the  $Cu-N_{a-pex}$  bond and the third phenolic group remains unattached to the central metal centre (Cu2)

$$\begin{split} 3[\text{H6TrenSalCu}]^+ + \text{La}(\text{NO}_3)_3 &\rightarrow [(\text{H6TrenSal})_2\text{Cu}_3]^{2+} \\ &+ [\text{H6TrenSalLa}(\text{NO}_3)_3] \end{split} \tag{1}$$

The appearance of this copper motif suggests that there can be competition for the H6TrenSal moiety when lanthanum is introduced into the mixture. In this instance some displacement of copper by lanthanum takes place (equation 1). In contrast to copper the products obtained from the reaction of [(H6Tren5BrSal)Zn] with gadolinium and cerium nitrate were all lanthanoid based. With gadolinium we retrieved [(H6Tren5BrSal)Gd(NO<sub>3</sub>)<sub>3</sub>] where the trivalent lanthanoid coordinates to the external O3 motif of the polydentate ligand and didentate with the three nitrate ligands (Fig. 6). Species similar to this have been reported previously [10]. The significance of this metal complex to this study is the cavity that remains within the ligand. Although it is clearly large enough to continue accommodating the zinc, the ligand is now devoid of zinc. It is unlikely that the differences between nickel and zinc arise from the Lewis acidity of these metals. A plausible explanation lies in the preferred geometries of the two metals. Zinc, having a preference for lower coordination numbers allows the secondary amines more latitude to protonate. This allows a build-up of positive charge in the vicinity of the cavity which assists the migration of the zinc from the pocket and prevents the ingress of the lanthanoid. A contribution to this process may also stem from the manner in which the lanthanoid arranges the oxygen donors such that the pocket is held in an open configuration weakening the zinc-donor interactions. Taken together the products obtained from these copper and zinc precursors can be used to support the process described by equation 1. However the analogous trizinc species has not been isolated from our reactions. Instead only monomeric starting material, {(H6TrenSal)Zn], and the lanthanum complex shown are obtained.

The reaction of [(H6TrenSal)Zn]<sup>+</sup> with lanthanoids was investigated further using cerium nitrate to confirm the reaction profile. However, in this instance we obtained a nine coordinate cerium complex (Fig. 7). It would seem that on complexing to the exterior of the ligand the cerium oxidises and divests itself of the attendant nitrates and becomes internalised within the ligand (Fig. 7). The internalisation of lanthanoids by this family of ligand has been reported previously for the eight coordinate species [H6TrenSalGd]<sub>2</sub> [18]. However, coordination expansion in the manner observed here is a new and novel facet of cerium chemistry. At this stage



**Fig. 5.** The X-ray crystal structure of  $[(H6TrenSal)_2Cu_3]$  4NO<sub>3</sub>. The data failed to refine to an acceptable degree. Thus only the identity of the compound and the connectivity of the atoms can be confirmed. The data was not deposited with the CCDC but can be found for inspection in the supplementary material.



**Fig. 6.** The X-ray crystal structure of [(H6Tren5BrSal)Gd(NO<sub>3</sub>)<sub>3</sub>]. The thermal ellipsoids are given at 50% probability.



**Fig. 7.** The X-ray crystal structure of  $[[(H6TrenSal)Ce]_2-\mu^2-O_2]$  Selected bond lengths (Å) Ce–O4 2.333(5), Ce–O4<sup>2</sup> 2.366(5): Bond angles (°) O–Ce–O, 37.42; Ce–O–Ce, 142.58. The thermal ellipsoids are at 50%.

the complex is formulated as the peroxo complex [(H6Tren-Sal)Ce(IV)]<sub>2</sub>- $\mu^2$ -O<sub>2</sub>]. The separation between the oxygens (O4–O4 Fig. 7) is found to be 1.508 Å. This value comes towards the lower edge of the range for this type of complex [19–22]. Similarly the values do not support the presence of two independent bridging hydroxides as the distances here are typically above 2.4 Å [23–25]. However, the observed room temperature magnetic moment of this complex is found to be 1.3 BM which is lower than typically (~2.2 BM) found for cerium(III) complexes [26]. Complexes of this type have been reported to be mixed valent (Ce(III)/Ce(IV)) [27] and as such, the structure of the complex could be reformulated as a  $\mu^2$ -superoxo complex. The true identity of this species is worthy of further study as compounds of this type are assuming some importance in biotechnology for DNA hydrolysis [28].

The study was initiated to investigate the synthesis of mixed copper lanthanoid species using the precedent set by Orvig et al. in their studies of mixed nickel complexes. While the desired species failed to form the reactions being employed seem to allow the synthesis of some intriguing lanthanoid motifs.

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#### Appendix A. Supplementary data

X-ray crystallographic data in CIF format. This material is available free of charge via the internet at http://www.ccdc.cam.ac.uk quoting deposition numbers 684063 - 684074. Data was collected for [(H6TrenSal)<sub>2</sub>Cu<sub>3</sub>] 4NO<sub>3</sub> and [(H6TrenSal)Cu] NO<sub>3</sub>. However, the data failed to refine to an acceptable degree. This data was not deposited with the CCDC but can be found for inspection in the supplementary material. Also shown are the expected and found mass spectral data for the key ions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.06.026.

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