DALTON
FULL PAPER

Metal mediated degradation of tripodal imine–phenol ligands: designer ligands with metal ion designers

Pravat Bhattacharyya, Jonathan Parr * and Alexandra M. Z. Slawin

Department of Chemistry, Loughborough University, Loughborough, Leics., UK LE11 3TU

Received 17th July 1998, Accepted 6th August 1998

Hydrated metal salts, M = Cu or Zn, promoted partial hydrolysis of tripodal imine–phenol ligands $N[CH_2CH_2N{=}CHC_6H_3(R)OH\text{-}2]_3$ (H_3L) with concomitant formation of complexes of M^{II} with the N-bearing fragment of the ligand which remains. With zinc(II) tetrafluoroborate hydrate, complexes $[Zn\{N[CH_2CH_2N{=}CHC_6H_3\text{-}(R)O\text{-}2](CH_2CH_2NH_2)_2\}[BF_4]$ (hereafter $[ZnL'][BF_4]$) where R = H **1**, 3-OCH_3 **2**, 5-Br **3** or 5-NO_2 **4** were obtained; the crystal structure of **3** reveals that the zinc centre has a distorted trigonal bipyramidal geometry, with an $[N_3]$ trigonal plane and the salicylidene oxygen and tertiary nitrogen atom of L′ occupying the axial positions. The corresponding reaction of H_3L with copper(II) perchlorate hexahydrate proceeded with analogous hydrolysis to yield dicationic complexes $[Cu(HL')][ClO_4]_2$ where R = H **5**, 3-OCH_3 **6**, 5-Br **7** or 5-NO_2 **8**. The crystal structure of **8**·MeOH revealed protonation at a pendant aminoethyl nitrogen atom of L′, resulting in a four-co-ordinate square planar $[N_3O]$ donor set for Cu^{II} with the salicylidene oxygen atom *trans* to the tertiary nitrogen atom. In addition, for R = 5-NO_2, crystals of a second compound **8a**·MeOH, isolated from the mother-liquor of **8**, have been shown by X-ray crystallography to be a five-co-ordinate complex $[CuL'][ClO_4]$ with a trigonal bipyramidal arrangement of the $[N_4O]$ donor atoms at the copper centre, isomorphous with the zinc complexes.

In the area of research which is concerned with the preparation of designer ligands, which is to say ligands which show a high degree of competence and selectivity for a particular metal or a particular application, most efforts have been directed towards preparing ligands from a first principles approach. The argument could be made, however, that template reactions are the most efficient routes to designer ligands, since the metal participates in the process of ligand assembly. In the examples reported here, we have used a templated destruction, rather than a template assembly, to prepare complexes.

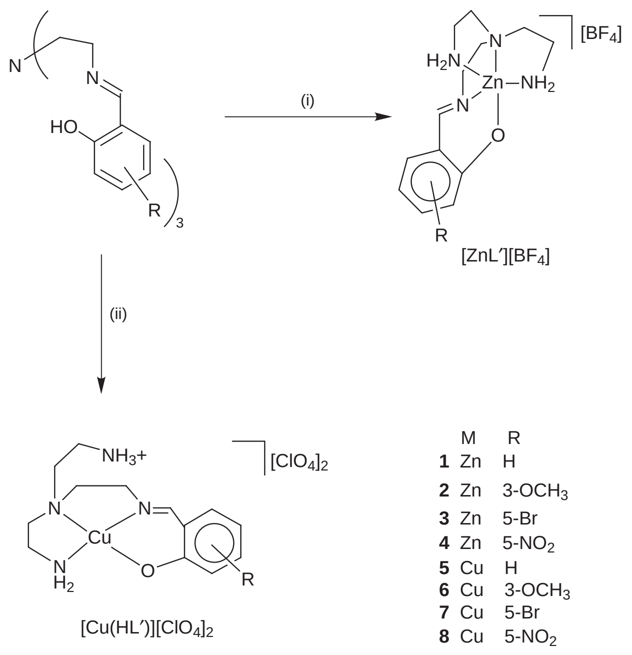
Tripodal imine phenol ligands $N[CH_2CH_2N{=}CHC_6H_3(R)\text{-}OH\text{-}2]_3$ (H_3L), prepared from the condensation of tris(2-aminoethyl)amine (tren) and substituted salicylaldehydes, have a well explored co-ordination chemistry.[1–6] Complexation of trivalent metal cations by triply deprotonated ligands L^{3-} gives rise to an octahedral $[N_3O_3]$ co-ordination sphere at the metal centre, with additional participation of the apical nitrogen atom to give an $[N_4O_3]$ donor set for larger cations such as lanthanides and Bi^{III}. Divalent metals with such ligands have, in contrast, received less attention. We have recently described the unusual co-ordination polyhedra produced at Pb^{II} using H_3L, in which the non-co-ordination of imine nitrogen atoms or phenolate oxygen atoms is a prominent feature in the solid state,[7,8] while salts of Cu^{II} and Sn^{II} are reported to promote hydrolysis of the imine bonds in related tripodal ligands.[9–11] We describe here the partial hydrolysis of such ligands at the C=N bonds by Zn^{II} or Cu^{II} for tripodal imine phenol ligands with a variety of substituent groups R, leading to five- and four-co-ordinate complexes respectively.

Results and discussion

Synthesis and spectroscopic characterisation of metal complexes

The reaction between zinc(II) tetrafluoroborate and imine phenol ligands H_3L proceeds in acetonitrile at room temperature with partial hydrolysis of the imine bonds according to Scheme 1, leading to yellow-orange cationic complexes $[ZnL'][BF_4]$ **1**–**4**. The ^1H NMR spectra of **1**–**4** (CD_3CN) show signals for the remaining salicylidene moiety [δ(CH=N) 8.2–8.5] and the ethylene groups of L′ with intensities consistent with their formulation. These are further corroborated by elemental analyses and FAB^+ mass spectrometry, the peak of highest intensity corresponding to $[ZnL']^+$. The infrared spectra of **1**–**4** (KBr discs) show small variations (*ca.* 0–5 cm^{-1}) in ν(C=N) from the free H_3L values with prominent ν(N–H) vibrations due to the reformed amine groups appearing as medium-strong intensity bands in the region 3400–3100 cm^{-1}.

Copper(II) perchlorate hexahydrate also promotes partial hydrolysis of H_3L in methanol under ambient conditions, Scheme 1; in contrast to the monocationic complexes isolated



	M	R
1	Zn	H
2	Zn	3-OCH3
3	Zn	5-Br
4	Zn	5-NO2
5	Cu	H
6	Cu	3-OCH3
7	Cu	5-Br
8	Cu	5-NO2

Scheme 1 The preparation of complexes **1**–**8a**. (i) $Zn(BF_4)_2{\cdot}nH_2O$, MeCN, room temperature (r.t.); (ii) $Cu(ClO_4)_2{\cdot}6H_2O$, MeOH, r.t.

using Zn^{II}, elemental analyses suggest two perchlorate counter ions are present, confirmed in the case of R = 5-NO_2 **8** by X-ray crystallography. Owing to the lower solubility of **8** compared with the other copper complexes **5**–**7**, recrystallisation of precipitates from the reaction mixture using methanol–diethyl ether realises a further quantity of the complex; additionally minor quantities of a secondary product **8a**, separated from the bulk compound as turquoise crystals suitable for X-ray study, have been isolated. The molecular structure of **8a**·MeOH reveals the complex to be a five-co-ordinate species [CuL′][ClO_4]. As found in the zinc complexes **1**–**4**, the dark green copper complexes **5**–**8** show small changes in their IR spectra [*ca.* 0–5 cm^{-1} for ν(C=N)] from the values for H_3L, while the ν(NH) vibrations are notably broader than for **1**–**4**.

Complexes containing both amine and imine functionalities derived from tripodal ligands have been reported from Cu^{II}-catalysed hydrolyses of $N[CH_2CH_2N{=}C(Me)C_6H_4OH\text{-}2]_3$ or $N[CH_2CH_2N{=}CHC_5H_4N]_3$.[9,11] In each case, two of the three imine bonds in the ligand are hydrolysed to NH_2 groups under the reaction conditions employed, giving four- and five-co-ordinate complexes respectively. Notably in this context, a ten-co-ordinate lanthanum(III) complex [LaL′$_2$][CF_3SO_3] has been prepared from the condensation reaction between [La(tren)$_2$][CF_3SO_3]$_3$ and 1 equivalent of salicylaldehyde;[13] using 2 or 3 equivalents of salicylaldehyde leads to [La(H_3L)] (R = H). Costes and co-workers[14] have recently reported Cu^{II}-mediated template synthesis of ‘half-unit’ amine–imine ligands resulting from condensation of one amine group in a variety of 1,*n*-diamines with 1 equivalent of salicylaldehyde in the presence of imidazole or pyridine; the crystal structure of [Cu($H_2NCH_2CH_2N{=}CHC_6H_4O$-2)(Him)][$ClO_4$] (Him = imidazole) confirms in this case a tridentate co-ordination of the ‘half-unit’ ligand through the phenolate oxygen, primary amine and imine nitrogen atoms. The reaction of tin(II) chloride dihydrate with $N(CH_2CH_2N{=}CHC_6H_4OH\text{-}2)_3$ leads, in contrast to Cu^{II}, to extensive destruction of the imine phenol, yielding the component triamine and aldehydes, accompanied by oxidation of the metal to Sn^{IV}.[10] There is in this latter example no evidence from ^1H NMR spectroscopy for any partially hydrolysed imine phenol species in the reaction mixture. On the basis that the complexes **1**–**8** contain one unhydrolysed imine phenol group, which has been reported as stable under strongly acidic conditions,[9] we suggest that co-ordination and so deprotonaton of one arm of the tripodal ligand to M^{2+} generates small quantities of $H_3O^+X^-$ (X = ClO_4 or BF_4) *in situ*, which catalyses the hydrolysis of the remaining unbound salicylidene arms back to amine groups more rapidly than the cascade of complexations of the remaining salicylidene units. The amine groups so generated then bind to the metal centre in preference to any condensation with free salicylaldehydes present in solution.

Single crystal X-ray diffraction studies

Single crystal X-ray diffraction studies upon a crystal of complex **3** (R = 5-Br) grown from acetonitrile–diethyl ether reveal a pseudo trigonal bipyramidal arrangement at zinc (Fig. 1) comprising two aminoethyl nitrogen atoms N(13), N(23) and an imine group N(3) in the trigonal plane, the apical positions being occupied by the tripodal nitrogen atom N(1) and O(6) of the salicylidene moiety. There are two crystallographically independent molecules of **3** in the unit cell, with 0.25 molecules of water per zinc(II) atom; values of structural parameters for the second molecule are given in the text and Table 1 in square brackets. [For the second independent molecule the zinc atom is labelled Zn(2), with all other atom descriptors being thirty higher in value than in the first molecule, so N(1) in the first molecule is N(31) in the second molecule.] There are significant distortions from idealised trigonal bipyramidal geometry in **3**, Zn(1) being displaced by 0.32 [0.33] Å from the mean N(3)–N(13)–N(23) plane, with the N(1)–Zn(1)–O(6) axis being 171.7(3)° [172.4(3)°]. The two independent molecules of **3** in the unit cell are associated into dimer pairs by hydrogen-bonding interactions between the amine protons and the oxygen atom of the adjacent cation, and also by secondary interactions with the disordered tetrafluoroborate anions (Fig. 2) [H(13A)···O(36) 2.16(1) Å, N(13)–H(13A)···O(36) 170°; O(6)···H(43A) 2.09(1) Å, O(6)···H(43A)–N(43) 169°; H(23B)···F(4) 2.29(1) Å, N(23)–H(23B)···F(4) 165°; F(1′)···H(53B) 2.14(1) Å, F(1′)···H(53B)–N(53) 159°]. The structure of the cation in **3** can be usefully compared with that of the tris(2-aminoethyl)amine complex [Zn(tren)Cl]Cl·3H_2O, in which the tertiary nitrogen atom occupies an axial position *trans* to Cl^-, the three primary amine nitrogens collectively forming the trigonal equatorial plane.[14] As found in **3**, the Zn–N_{apical} distance [2.265(2) Å] in the tren complex is distinctly longer than the Zn–N_{eq} lengths [2.050(2)–2.076(3) Å], with a similar displacement of the zinc atom from the equatorial plane [N_{apical}–Zn–N_{eq} 80.42(9)–81.13(7)°]; the N_{apical}–Zn–Cl angle is closer to linearity, being 177.15(6)°.

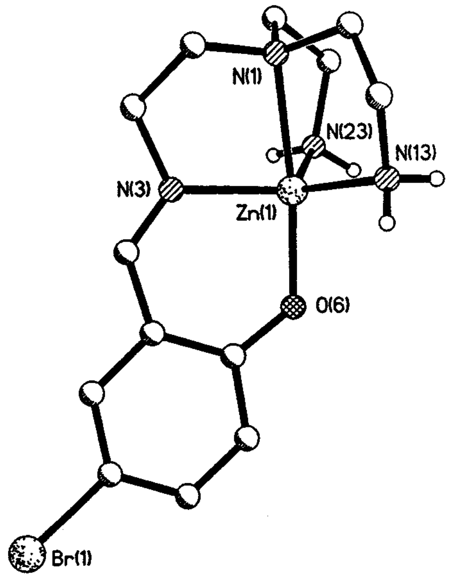


Fig. 1 Crystal structure of the cation in complex **3**·0.25H_2O (hydrogen atoms bound to carbon omitted for clarity).

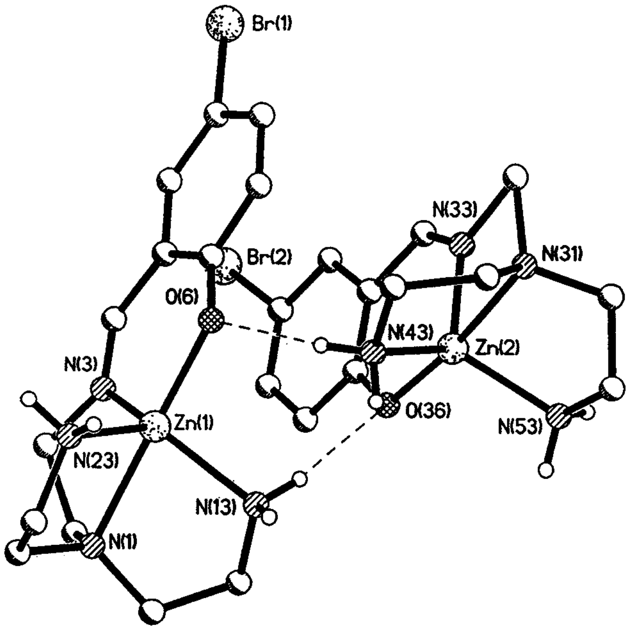


Fig. 2 Hydrogen-bonding interactions between the amine protons and the phenolate oxygen atoms in the two independent molecules of complex **3** (hydrogen atoms bound to carbon omitted for clarity).

Table 1 Selected bond lengths (Å) and angles (°) for compounds **3**, **8** and **8a** (estimated standard deviations in parentheses)

	3*	**8**	**8a**
M(1)–N(1)	2.263(7) [2.258(7)]	2.064(4)	2.043(5)
M(1)–N(3)	2.021(7) [2.029(7)]	1.944(4)	1.964(5)
M(1)–N(13)	2.064(7) [2.058(7)]	1.997(4)	2.118(6)
M(1)–N(23)	2.070(7) [2.064(8)]	—	2.096(6)
M(1)–O(6)	1.993(5) [1.993(6)]	1.926(3)	1.930(4)
N(3)–C(4)	1.282(12) [1.256(12)]	1.252(6)	1.274(5)
N(13)–M(1)–N(1)	81.4(3) [81.2(3)]	86.2(2)	83.6(3)
N(1)–M(1)–N(3)	80.2(3) [80.4(3)]	85.2(2)	85.0(2)
O(6)–M(1)–N(1)	171.7(3) [172.4(3)]	176.9(2)	177.2(2)
O(6)–M(1)–N(3)	92.5(3) [92.1(3)]	92.8(2)	92.2(2)
O(6)–M(1)–N(13)	99.5(3) [101.6(3)]	95.0(2)	97.8(2)
O(6)–M(1)–N(23)	105.5(3) [103.8(3)]	—	97.6(2)
N(1)–M(1)–N(23)	81.1(3) [80.9(3)]	—	84.4(2)
N(3)–M(1)–N(13)	122.7(3) [121.1(3)]	162.7(2)	124.7(3)
N(23)–M(1)–N(13)	117.6(3) [116.7(3)]	—	105.3(3)
N(3)–M(1)–N(23)	112.2(3) [114.7(3)]	—	127.1(3)

* Two crystallographic independent cations in unit cell, values for second molecule given in square brackets.

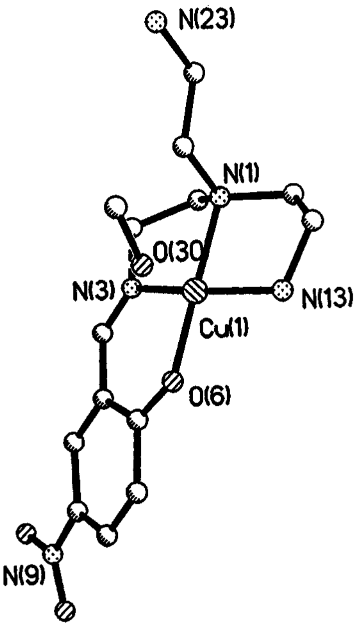


Fig. 3 Crystal structure of the cation in complex **8**·MeOH (hydrogen atoms omitted for clarity).

Crystals of complex **8** suitable for X-ray study were grown from methanol–diethyl ether. The Cu(1) co-ordination sphere of **8** (Fig. 3), which crystallises with one molecule of methanol solvate, comprises tertiary and primary nitrogen atoms, N(1) and N(13) respectively, and the N(3) and O(6) atoms of the chelating salicylidene moiety in a distorted square-planar arrangement, with N(1) being *trans* to O(6); the nitrogen atom N(23) of the unbound arm is protonated, and disposed away from the metal centre [Cu(1)···N(23) 5.32 Å] due to charge effects. The complex is isostructural with that reported by Fenton *et al.*[9] from the reaction of copper(II) perchlorate with the related tripod $N[CH_2CH_2N{=}C(Me)C_6H_4OH\text{-}2]_3$; the analogous bond lengths and angles in the two structures are found to be in close agreement. For **8** the imine nitrogen N(3) provides the shortest Cu–N distance [Cu(1)–N(3) 1.944(5) Å]; the *cis* N–Cu–X angles (X = phenolate O or N) are in the range 85.2(2)–95.0(2)°, a significant deviation from idealised square-planar geometry, with Cu(1) being displaced by 0.15 Å above the $[N_3O]$ co-ordination plane. There is a weak intramolecular hydrogen-bonding interaction between one of the hydrogen atoms of N(23) and a perchlorate counter ion [H(23a)···O(14) 2.24 Å, N(23)–H(23a)···O(14) 126°] and also a stronger interaction of a perchlorate oxygen atom O(11) with a hydrogen atom H(23B′) from N(23′) of a neighbouring cation [H(23B′)···O(11) 1.99 Å, N(23′)–H(23B′)···O(11) 171°]. For N(1) the C–N(1)–C angles [112.7(5)–114.1(5)°] are significantly larger than C–N(1)–Cu(1) [103.1(3)–109.3(3)°].

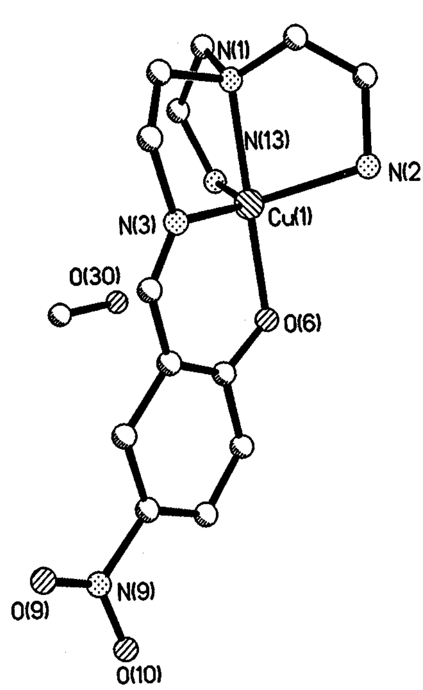


Fig. 4 Crystal structure of the cation in complex **8a**·MeOH (hydrogen atoms omitted for clarity).

Complex **8a** (Fig. 4), which crystallises with one molecule of methanol solvate, has the same geometry at Cu(1) as the zinc(II) complex **3**; the unbound protonated aminoethyl arm of **8** has been deprotonated and co-ordinates to Cu(1), giving a trigonal bipyramidal $[N_4O]$ donor set at the metal. The Cu(1)–N distances to the apical and imine nitrogen atoms N(1) and N(3) are essentially unchanged from **8**, the Cu(1)–N(13) length [2.118(6) Å in **8a**, 1.997(4) Å in **8**] exhibiting a distinct elongation by *ca.* 0.12 Å. Comparisons of the bonding parameters in **8a** and the zinc complex **3** are more informative. The M(1)–O(6) and M(1)–N(1) lengths in **8a** are shortened by *ca.* 0.06 and 0.22 Å compared with **3** {M(1)–O(6) 1.930(4) Å in **8a**, 1.993(5) [1.993(6)] Å in **3**; M(1)–N(1) 2.043(5) Å in **8a**, 2.263(7) [2.258(7) Å] in **3**}, with the N(1)–M(1)–O(6) axis closer to linearity in **8a**, being 177.2(2)° *cf.* 171.7(3) [172.4(3)°] for **3**. Compression of the M(1)–N(3) bond in **8a** causes expansion of the equatorial N(3)–M(1)–N_{amine} angles compared with **3** {N(3)–M(1)–N(13) 124.7(3)° in **8a**, 122.7(3) [121.1(3)°] in **3**; N(3)–M(1)–N(23) 127.1(3)° in **8a**, 112.2(3) [114.7(3)°] in **3**}, and some lengthening of the M(1)–N(13) and M(1)–N(23) distances. The Cu(1) atom in **8a** is displaced below the equatorial N(3)–N(13)–N(23) co-ordination plane by 0.2 Å, 0.12 Å less than in the zinc(II) complex **3**; the *cis* N(1)–Cu–N_{amine} angles [83.6(2)–85.0(2)°] are comparable to the corresponding angles in [Cu(tren)Ade]Cl,[15,16] where HAde = adenine [83.3(4)–84.6(4)°]. The perchlorate counter ion in **8a** is not involved in hydrogen bonding with the neutral NH_2 groups of the cationic complex.

Conclusion

The Lewis acids Zn^{II} and Cu^{II} can be used to promote the hydrolysis of imine bonds in tripodal imine–phenols, to yield multidentate ligands with four distinct donor atom types. In addition, the highly selective nature of this degradation reaction, yielding the twice hydrolysed product in high yield, offers the intriguing possibility of preparing asymmetric tripodal

Table 2 Details of X-ray data collections and refinements for compounds **3**, **8** and **8a**

	3·0.5H_2O	**8**·CH_3OH	**8a**·CH_3OH
Empirical formula	$C_{13}H_{20}BBrF_4N_4OZn$	$C_{14}H_{25}Cl_2CuN_5O_{12}$	$C_{14}H_{24}ClCuN_5O_8$
M	484.92	589.83	489.37
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Crystal colour	Yellow	Dark green	Turquoise
Space group	$P2_1/c$	$Pbna$[a]	$P2_1/c$
a/Å	20.624(1)	10.984(1)	7.463(1)
b/Å	13.701(1)	15.146(1)	24.796(1)
c/Å	14.946(1)	27.342(1)	11.361(1)
β/°	105.74(1)		107.89(1)
U/Å^3	4065.02(9)	4548.4(2)	2000.82(8)
Z	8	8	4
D_c/Mg m^{-3}	1.585	1.723	1.625
μ/mm^{-1}	3.218	1.266	1.278
F(000)	1940	2424	1012
Crystal size/mm	0.14 × 0.14 × 0.14	0.08 × 0.24 × 0.44	0.1 × 0.1 × 0.1
θ range/°	1.03–23.28	1.49–23.43	1.64–23.30
h,k,l ranges	−22 to 21, −15 to 15, −10 to 16	−12 to 8, −16 to 16, −30 to 30	−6 to 8, −27 to 26, −12 to 12
Total data	17523	18364	8721
Unique data (R_{int})	5855 (0.0380)	3317 (0.1785)	2891 (0.0456)
No. of parameters	447	310	272
Goodness of fit on F^2	0.898	0.835	0.932
$R1$, $wR2$ [$I > 2\sigma(I)$][b]	0.0753, 0.2080	0.0568, 0.1158	0.0506, 0.1261
Extinction coefficient	—[c]	0.0002(2)	0.0010(8)
Maximum, minimum $\Delta\rho$/e Å^{-3}	1.408, −0.903	1.257, −0.936	0.798, −0.430

[a] A non-standard setting of $Pbcn$ (no. 60). [b] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|)$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [c] Owing to disorder of the BF_4^- anion manual extinction of reflections used rather than extinction parameter. No absorption corrections were applied for structure **8a**; semiempirical corrections from ψ scans were made for **3** and **8**.

ligands. If the L′ formed here can be displaced from the metals, then the pendant arms could be further substituted in a variety of ways to yield (2 + 1) tripods, with non-equivalent legs. This avenue of research is currently being pursued in our laboratory.

Experimental

Materials

All complexation reactions were carried out under an atmosphere of oxygen-free nitrogen; acetonitrile and diethyl ether were dried and distilled from calcium hydride and sodium–benzophenone respectively, methanol was dried by storage over 4A molecular sieves. Absolute ethanol (100%) and hexanes were of reagent grade and used as received. Ligands H_3L were prepared by condensation of the appropriate salicylaldehyde derivative (Aldrich) with tren in ethanol;[1,12] hydrated zinc(II) tetrafluoroborate (Strem, 98%) and copper(II) perchlorate hexahydrate (BDH) were used as received. **CAUTION**: although we have encountered no difficulties, perchlorate salts are potentially explosive and must be handled with care.

Physical measurements

Infrared spectra (pressed KBr discs) were recorded on a Perkin-Elmer System 2000 NIR FT-Raman spectrometer, microanalyses were performed by the University of Loughborough Analytical Service (Perkin-Elmer 2400 CHN elemental analyser). The ^1H NMR spectra (250.13 MHz) for complexes **1**–**4**, recorded in CD_3CN (Aldrich, 99.6 atom% D) on a Bruker AM250 spectrometer, were referenced to external tetramethylsilane (δ 0) using the high-frequency positive convention. Fast atom bombardment mass spectra (positive mode, 3-nitrobenzyl alcohol matrix) were obtained by the EPSRC National Mass Spectrometry Service Centre, Swansea.

X-Ray crystallography

The crystal structures of complexes **3**, **8** and **8a** were determined at 298 K using a Siemens SMART diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω scans. The crystal data, a summary of the data collections and the structure refinements for these compounds are given in Table 2. All structures were solved by direct methods and all of the non-hydrogen atoms refined with anisotropic displacement parameters; the hydrogen atoms bound to carbon were included in calculated positions (C–H 0.95 Å) with a fixed isotropic displacement parameter. The hydrogen atoms associated with N(13) and N(23) were not located and were idealised (N–H 0.90 Å for **3**, 0.98 Å for **8** and **8a**). The hydrogen atom H(30) associated with O(30) of the methanol solvate in the structures of **8** and **8a** were located by difference maps and allowed to refine isotropically with no distance restraint. Refinement was by full-matrix least-squares methods on F^2; calculations were performed using the program SHELXTL PC.[17]

CCDC reference number 186/1120.

Preparation of complexes

Complexes **1**–**4** were all prepared by the same general route, given here for **3**, R = 5-Br. Hydrated zinc(II) tetrafluoroborate (0.065 g, 0.27 mmol) and tris[2-(5-bromosalicylideneamino)-ethyl]amine (0.19 g, 0.27 mmol) were stirred together in acetonitrile (15 cm^3) for 24 h. The yellow solution was concentrated to *ca.* 3 cm^3 under reduced pressure, whereafter diffusion of diethyl ether vapour into the acetonitrile solution gave 0.084 g (65%) of $[Zn\{N(CH_2CH_2N{=}CHC_6H_3Br\text{-}5\text{-}O\text{-}2)(CH_2CH_2NH_2)_2\}][BF_4]$ **3** as a yellow microcrystalline solid. Isolated yields were typically 45–70% based on Zn for **1**–**4**.

1 (R = H) [Found (Calc. for $C_{13}H_{21}BF_4N_4OZn$): C, 39.6 (39.9); H, 5.1 (5.3); N, 13.6 (14.0)%]: δ_H 8.45 (1 H, s, CH=N), 7.29 (1 H, dd, J 7 and 1.5, C_6H_4), 7.23 (1 H, dm, C_6H_4), 6.69 (1 H, dm, C_6H_4), 6.62 (1 H, dt, J 1 and 8, C_6H_4), 3.69 (2H, t, J 6 Hz, CH_2) and 3.0–2.7 (m, CH_2 and NH); IR (cm^{-1}) ν(NH) 3360m, 3255m, 3151m, ν(CN) 1641s, ν(BF_4) 1056vs; FAB *m*/*z* 313, $M^+ - BF_4$.

2 (R = 3-OCH_3) [Found (Calc. for $C_{14}H_{23}BF_4N_4O_2Zn$): C, 38.7 (39.0); H, 5.1 (5.4); N, 12.6 (13.0)%]: δ_H 8.20 (1 H, s, CH=N), 6.77 (1 H, d, J 5, C_6H_3), 6.74 (1 H, d, J 5, C_6H_3), 6.41 (1 H, t, J 5, C_6H_3), 3.69 (3 H, s, CH_3), 3.31 (2 H, t, J 6 Hz, CH_2) and 3.0–2.7 (m, CH_2 and NH); IR (cm^{-1}) ν(NH) 3231s, 3127s, ν(CN) 1642s, ν(BF_4) 1058vs; FAB *m*/*z* 343, $M^+ - BF_4$.

3 (R = 5-Br) [Found (Calc. for $C_{13}H_{20}BBrF_4N_4OZn$): C, 32.7 (32.5); H, 4.3 (4.2); N, 11.4 (11.7)%]: δ_H 8.39 (1 H, s, CH=N), 7.36 (1 H, dd, *J* 3 and 9, C_6H_3), 7.30 (1 H, d, *J* 3, C_6H_3), 6.63 (1 H, d, *J* 9, C_6H_3), 3.70 (2 H, t, *J* 6 Hz, CH_2) and 3.1–2.7 (m, CH_2 and NH); IR (cm^{-1}) ν(NH) 3364w, 3275m, ν(CN) 1643s, ν(BF_4) 1059vs; FAB: *m*/*z* 393, $M^+ - BF_4$.

4 (R = 5-NO_2) [Found (Calc. for $C_{13}H_{20}BF_4N_5O_3Zn$): C, 34.8 (35.0); H, 4.3 (4.5); N, 15.4 (15.7)%] δ_H 8.55 (1 H, s, CH=N), 8.27 (1 H, d, *J* 3 , C_6H_3), 8.09 (1 H, dd, *J* 3 and 9, C_6H_3), 6.69 (1 H, d, *J* 9, C_6H_3), 3.76 (2 H, t, *J* 6 Hz, CH_2) and 3.0–2.7 (m, CH_2 and NH); IR (cm^{-1}) ν(NH) 3346m, 3294m, ν(CN) 1652s, ν(BF_4) 1058vs; FAB *m*/*z* 358, $M^+ - BF_4$.

Complexes **5**–**8** were all prepared by the same general route, given here for **7**, R = 5-Br. Copper(II) perchlorate hexahydrate (0.11 g, 0.3 mmol) and tris[2-(5-bromosalicylideneamino)ethyl]amine (0.21 g, 0.3 mmol) were stirred together in methanol (10 cm^3) for 48 h, giving a dark green solution. The solution was concentrated to 3 cm^3 under reduced pressure, whereafter diffusion of diethyl ether vapour into the methanolic solution gave 0.15 g of **7** as dark green microcrystals. Isolated yields were typically 60–70% based on Cu for **5**–**8**. For R = 5-NO_2 **8** a blue-green precipitate was collected from the reaction by centrifugation; recrystallisation from methanol–diethyl ether gave a further crop of **8** and, separated manually under the microscope, a small quantity (*ca.* 3 mg) of turquoise crystals **8a**·MeOH suitable for X-ray analysis.

5 (R = H) [Found (Calc. for $C_{13}H_{21}Cl_2CuN_4O_9$): C, 30.3 (30.6); H, 3.9 (4.1); N, 10.6 (11.0)%]: IR (cm^{-1}) ν(NH) 3338 (br), 3175 (br), ν(CN) 1639s, ν(ClO_4) 1089vs, 627s; FAB *m*/*z* 312, $M^+ - 2ClO_4$; UV/VIS (MeOH) λ_{max} 622 nm, ε 161 dm^3 mol^{-1} cm^{-1}.

6 (R = 3-OCH_3) [Found (Calc. for $C_{14}H_{24}Cl_2CuN_4O_{10}$): C, 37.2 (31.0); H, 4.7 (4.5); N, 8.6 (10.3)%]: IR (cm^{-1}) ν(NH) 3337 (br), 3252 (br), ν(CN) 1637s, ν(ClO_4) 1083vs, 623s; FAB *m*/*z* 342, $M^+ - 2ClO_4$; UV/VIS (MeOH) λ_{max} 614 nm, ε 143 dm^3 mol^{-1} cm^{-1}.

7 (R = 5-Br) [Found (Calc. for $C_{13}H_{21}BrCl_2CuN_4O_9$): C, 27.8 (27.2); H, 3.9 (3.7); N, 9.5 (9.8)%]: IR (cm^{-1}) ν(NH) 3338 (br), 3228 (br), ν(CN) 1639s, ν(ClO_4) 1090vs, 625s; FAB *m*/*z* 392, $M^+ - 2ClO_4$; UV/VIS (MeOH) λ_{max} 614 nm, ε 130 dm^3 mol^{-1} cm^{-1}.

8 (R = 5-NO_2) [Found (Calc. for $C_{13}H_{21}Cl_2CuN_5O_{11}$): C, 28.2 (28.0); H, 4.1 (3.8); N, 12.4 (12.6)%]: IR (cm^{-1}) ν(NH) 3365 (br), 3210 (br), ν(CN) 1648s, ν(ClO_4) 1098vs, 626m; FAB *m*/*z* 357, $M^+ - 2ClO_4$; UV/VIS (MeOH) λ_{max} 610 nm, ε 165 dm^3 mol^{-1} cm^{-1}.

Acknowledgements

We are grateful to the EPSRC (P. B.) for financial support.

References

1 D. F. Cook, D. Cummins and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1976, 1369.
2 S. K. Chandra, P. Chakraborty and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1993, 863.
3 M. Kanesato, T. Yokoyama, O. Habashi, T. M. Suzuki and M. Shiro, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1297.
4 G. Hunter and N. Kilcullen, *J. Chem. Soc., Dalton Trans.*, 1989, 2115.
5 P. K. Bharadwaj, A. M. Lee, S. Mandal, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1994, **47**, 1799.
6 J.-P. Costes, F. Dahan, A. Dupuis, S. Lagrave and J.-P. Laurent, *Inorg. Chem.*, 1998, **37**, 153.
7 J. Parr, A. T. Ross and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, 1996, 1509.
8 J. Parr, A. T. Ross and A. M. Z. Slawin, *Polyhedron*, 1997, **16**, 2765.
9 D. E. Fenton, G. P. Westwood, A. Bashall, M. McPartlin and I. J. Scowen, *J. Chem. Soc., Dalton Trans.*, 1994, 2213.
10 J. Parr, A. T. Ross and A. M. Z. Slawin, *Inorg. Chem. Commun.*, 1998, **1**, 159.
11 R. M. Kirchner, C. Mealli, M. Bailey, N. Howe, L. P. Torre, L. J. Wilson, L. C. Andrews, N. J. Rose and E. C. Lingafelter, *Coord. Chem. Rev.*, 1987, **77**, 89.
12 J. A. Broomhead and D. J. Robinson, *Aust. J. Chem.*, 1968, **21**, 1365.
13 M. Kanesato, T. Yokoyama and T. M. Suzuki, *Chem. Lett.*, 1997, 93.
14 J.-P. Costes, F. Dahan, M. B. Fernandez Fernandez, M. I. Fernandez Garcia, A. M. Garcia Deibe and J. Sanmartin, *Inorg. Chim. Acta.*, 1998, **274**, 73.
15 A. Marzotto, D. A .Clemente and G. Valle, *Acta. Crystallogr., Sect. C*, 1994, **50**, 1451.
16 A. Marzotto, A. Ciccarese, D. A. Clemente and G. Valle, *J. Chem. Soc., Dalton Trans.*, 1995, 1461.
17 G. M. Sheldrick, SHELXTL, version 5.03, program for crystal structure solution, University of Göttingen, 1994.

Paper 8/05558K