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# The coordination chemistry of unsymmetric *N*-capped tripodal NO<sub>3</sub> ligands with iron(III), oxo-vanadium(V) and dioxo-molybdenum(VI) metal centres

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#### ABSTRACT

The synthesis and characterisation of iron(III)  $[Fe(L^1)]_2$  (**1**), oxo-vanadium(V)  $[VO(L^1)]$  (**2**) and dioxomolybdenum(VI)  $K[MOO_2(L^1)]$  (**3**) complexes supported by a partially unsymmetric *N*-capped tripodal NO<sub>3</sub> ligand (L<sup>1</sup>) are reported. Complexes **1** and **2** were prepared by reactions of a proligand  $[H_3L^1]$  and their corresponding metal precursor (FeCl<sub>3</sub> and VOCl<sub>3</sub>, respectively) in the presence of triethylamine in THF, while **3** was obtained in a similar manner by treating  $[MOO_2(acac)_2]$  (acac = acetylacetonate) with the same proligand and potassium hydroxide in methanol. The X-ray crystal structure of **1** illustrates a dimeric structure with a *bis*-( $\mu$ -phenoxo) Fe<sub>2</sub>O<sub>2</sub> diamond core, and each iron centre bears a rare NO<sub>4</sub> coordination sphere. The preparation of a previously unknown, fully unsymmetric *N*-capped tripodal NO<sub>3</sub> proligand  $[H_3L^2]$  featuring three different phenolic arms is also described. Reaction of  $[H_3L^2]$  with VOCl<sub>3</sub> yielded the oxo-vanadium(V) complex  $[VO(L^2)]$  (**4**). Complexes **2–4** exist as monomers in solution and were characterised by NMR (<sup>1</sup>H and <sup>13</sup>C), IR (for **3**), mass spectrometry, and elemental analysis.

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# 1. Introduction

The coordination chemistry and reactivity of both transitionmetal [1-10] and main-group complexes [11-14] containing tetradentate N-capped tripodal NO<sub>3</sub> ligands have attracted considerable research interests. This versatile class of ligands reacts with simple, commercially available metal precursors to give metal complexes which provide opportunities for investigations of catalysis as well as a number of organic transformations [15]. Symmetric triphenolamine ligands (type I, Fig. 1) have been extensively studied due to well established and easily accessible synthetic routes available for these ligands. Structural modifications of these tetradentate ligands are achievable by introducing various peripheral substituents onto the aromatic rings such that the electronic and steric environment around the metal centre can be readily modified. A triphenolamine ligand with a stereogenic centre incorporated into one of the methylene carbons has been reported recently and its potential applications in chiral recognition and asymmetric catalysis have been studied [16,17].

We have a particular interest in unsymmetric *N*-capped tripodal NO<sub>3</sub> tetradentate ligands with two different phenol pendant arms

(type II). These partially unsymmetric tetradentates featuring two different arm lengths can form  $\{5,6,6\}$  chelate ring-sizes upon complexation with metals. Recently, we have reported the synthesis and catalytic properties of a series of iron(III) complexes supported by this type of partially unsymmetric NO<sub>3</sub> ligands [18]. The same class of ligands have also been deployed to prepare titanium(IV) and zirconium(IV) complexes for studying catalytic polymerization of cyclic esters [19]. More recently, we have also reported a closely related tripodal ligand with a NO<sub>2</sub>S donor set. The latter was prepared by a synthetic route similar to that we used for the partially unsymmetric tripodal NO<sub>3</sub> ligands described above [20].

As part of a programme to explore the coordination chemistry of partially unsymmetric tripodal NO<sub>3</sub> ligands, we herein report the synthesis and characterisation of oxo-vanadium(V) and dioxomolybdenum(VI) complexes supported by a partially unsymmetric NO<sub>3</sub> ligand (L<sup>1</sup>). An iron(III) *bis*-( $\mu$ -phenoxo) dimer derived from L<sup>1</sup> was also isolated and structurally characterised by X-ray crystallography. The diiron complex possessed a Fe<sub>2</sub>O<sub>2</sub> diamond core with a rare five-coordinate NO<sub>4</sub> ligand environment around each iron(III) centre. In addition, a fully unsymmetric *N*-capped tripodal NO<sub>3</sub> ligand (type III) has also been prepared and its coordination chemistry with oxo-vanadium(V) was studied. This new ligand bears three different phenolate arms, and the difference in the substitution pattern on the two benzylic pendant arms introduces an entirely asymmetric environment around the metal centre.

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Fig. 1. Three types of N-capped tripodal NO<sub>3</sub> ligands. The coordination chemistry of the partially unsymmetric (type II) and fully unsymmetric (type III) ligands are described in this work.

## 2. Experimental

# 2.1. General information

All reactions were carried out using standard Schlenk-line techniques under an atmosphere of dinitrogen; workups were performed in air. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Methanol (MeOH) and triethylamine (Et<sub>3</sub>N) were distilled from magnesium methoxide and sodium, respectively. Silica gel (70-230 mesh) for flash column chromatography was purchased from Fluka. All other reagents were purchased from Aldrich and used as received. All <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Varian Mercury VX300 spectrometer (<sup>1</sup>H, 300 MHz and <sup>13</sup>C, 75.4 MHz) using CDCl<sub>3</sub> as solvent. Chemical shifts were relative to internal SiMe<sub>4</sub> ( $\delta$  = 0). Atmospheric pressure chemical ionisation (APCI) mass spectra were recorded on a Hewlett-Packard 1050 Series Mass Spectrometer. Elemental analyses were performed by the microanalysis laboratory of the Inorganic Chemistry Laboratory, University of Oxford, UK. N.N-bis(2-hydroxy-3,5-di*tert*-butylbenzyl)-N-(2'-hydroxy-5'-methyl-phenyl)amine (H<sub>3</sub>L<sup>1</sup>) [18] and 3,5-di-tert-butyl-2-hydroxybenzylbromide [18] were prepared according to literature procedures.

# 2.2. Synthesis of ligands

# 2.2.1. N-(2-hydroxybenzyl)-N-(2'-hydroxy-5'-methylphenyl)amine

To a solution of 2-hydroxy-5-methylaniline (1.22 g, 10.0 mmol) in MeOH (100 cm<sup>3</sup>) was added salicylaldehyde (1.07 cm<sup>3</sup>, 10.0 mmol). A bright orange Schiff-base product immediately formed and the mixture was kept stirring for 1 h at room temperature. NaBH<sub>4</sub> (0.76 g, 20.0 mmol) was slowly added and stirring was continued for a further period of 1 h. All the volatiles were removed under reduced pressure and the residue was quenched with water (50 cm<sup>3</sup>). The mixture was then neutralised with glacial acetic acid followed by extraction with  $CH_2Cl_2$  (3 × 30 cm<sup>3</sup>). The combined extracts were dried over anhydrous MgSO<sub>4</sub>, concentrated and pumped to dryness to give the product as a pale yellow viscous liquid. The compound was used without further purification. Yield: 2.23 g (97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.12-7.23 (m, 2H, ArH), 6.52-6.89 (m, 5H, ArH), 4.37 (s, 2H, ArCH<sub>2</sub>), 2.22 (s, 3H, ArCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  156.4, 142.6, 135.4, 130.7, 128.9, 128.5, 123.1, 120.9, 120.0, 116.5, 116.1, 114.6, 48.8, 21.1. MS (APCI): m/z 230 (15%)  $[M+H]^{+}$ .

2.2.2. N-(3,5-di-tert-butyl-2-hydroxybenzyl)-N-(2'-hydroxybenzyl)-N-(2"-hydroxy-5"-methylphenyl)amine ( $H_3L^2$ )

To a solution of *N*-(2-hydroxybenzyl)-*N*-(2'-hydroxy-5'-methylphenyl)amine (0.69 g, 3.0 mmol) in THF (30 cm<sup>3</sup>) at room temperature was added a solution of 3,5-di-tert-butyl-2-hydroxybenzylbr omide (0.90 g, 3.0 mmol) in THF (30 cm<sup>3</sup>) followed by triethylamine (1.25 cm<sup>3</sup>, 9.0 mmol). After heating under reflux overnight, the mixture was cooled, and the resulting white solid was filtered and discarded. The brown filtrate was concentrated with a rotary evaporator and the residue was chromatographed on a silica gel column using CHCl<sub>3</sub> as eluent. The second band was collected and concentrated to give a pale yellow solid. Yield: 0.97 g (72%). Mp: 80-82 °C. <sup>1</sup>H NMR:  $\delta$  7.06–7.12 (m, 3H, ArH), 6.94–6.98 (m, 2H, ArH), 6.72-6.83 (m, 4H, ArH), 4.16 (s, 2H, ArCH<sub>2</sub>), 4.13 (s, 2H, ArCH<sub>2</sub>), 2.20 (s, 3H, ArCH<sub>3</sub>), 1.33 (s, 9H, <sup>t</sup>Bu), 1.27 (s, 9H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  154.9, 152.2, 148.5, 141.0, 135.6, 134.9, 130.9, 129.4, 129.2, 126.2, 125.5, 123.3, 122.6, 122.3, 121.3, 120.2, 116.1, 115.8, 56.7, 56.3, 34.8, 34.1, 31.7, 29.7, 20.9. MS (APCI): m/z 448 (100%) [M+H]<sup>+</sup>. Anal. Calc. for C<sub>29</sub>H<sub>37</sub>NO<sub>3</sub>: C, 77.8; H, 8.3; N, 3.1. Found: C, 77.6; H, 8.2; N, 3.2%.

# 2.3. Synthesis of the complexes

#### 2.3.1. $[Fe(L^1)]_2(\mathbf{1})$

To a mixture of  $[H_3L^1]$  (0.56 g, 1.0 mmol) and FeCl<sub>3</sub> (0.16 g, 1.0 mmol) in THF (20 cm<sup>3</sup>) was added triethylamine (0.42 cm<sup>3</sup>, 3.0 mmol). After heating under reflux overnight, the mixture was cooled and filtered. The dark filtrate was concentrated with a rotary evaporator. The residue was chromatographed on a silica gel column using CHCl<sub>3</sub>/hexane (1:1) as eluent. The second band was collected and concentrated to give a black crystalline solid. Yield: 0.36 g (30%). Anal. Calc. for C<sub>74</sub>H<sub>100</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub>: C, 72.5; H, 8.2; N, 2.3. Found: C, 72.6; H, 8.4; N, 2.6%.

#### 2.3.2. $[vo(L^1)]$ (2)

To a solution of  $[H_3L^1]$  (1.12 g, 2.0 mmol) in THF (40 cm<sup>3</sup>) was added VOCl<sub>3</sub> (0.19 cm<sup>3</sup>, 2.0 mmol) followed by triethylamine (0.83 cm<sup>3</sup>, 6.0 mmol). The reaction mixture turned immediately to dark blue. After stirring at room temperature overnight, the reaction mixture was filtered and the dark blue filtrate was concentrated with a rotary evaporator. The residue was chromatographed on a silica gel column using CH<sub>2</sub>Cl<sub>2</sub> followed by ethyl acetate as eluents. The second band was collected and concentrated to give a dark blue crystalline solid. Yield: 0.91 g (73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.22 (d, *J* = 2.7 Hz, 2H, ArH), 7.14 (d, *J* = 1.5 Hz, 1H, ArH), 6.97 (d, *J* = 2.4 Hz, 2H, ArH), 6.88 (dd, *J* = 1.5, 8.3 Hz, 1H, ArH), 6.52 (d, *J* = 8.1 Hz, 1H, ArH), 4.08 (d, *J* = 13.5 Hz, 2H, ArCH<sub>2</sub>), 3.92 (d, *J* = 13.5 Hz, 2H, ArCH<sub>2</sub>), 2.29 (s, 3H, ArCH<sub>3</sub>), 1.54 (s, 18 H, <sup>t</sup>Bu), 1.28 (s, 18H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  164.8, 160.8, 145.8, 136.9, 134.9, 132.6, 128.6, 124.7, 123.8, 122.9, 122.5, 112.9, 58.7, 35.2, 34.6, 31.6, 30.0, 21.0. MS (APCI): *m/z* 624 (100%) [M+H]<sup>+</sup>. *Anal.* Calc. for C<sub>37</sub>H<sub>50</sub>NO<sub>4</sub>V: C, 71.2; H, 8.1; N, 2.2. Found: C, 71.5; H, 8.3; N, 2.5%.

#### 2.3.3. $K[MoO_2(L^1)]$ (3)

A colourless mixture of  $[H_3L^1]$  (0.56 g, 1.0 mmol) and KOH (0.056 g, 1.0 mmol) in MeOH  $(80 \text{ cm}^3)$  was added to  $[MoO_2(acac)_2]$ (0.33 g, 1.0 mmol). The mixture turned immediately to orange-red. After stirring at room temperature for 1 h, the solution was filtered and all the volatiles were removed on a rotary evaporator. The orange-red residue was redissolved in acetone (50 cm<sup>3</sup>) and the solution was stirred for 15 min. An insoluble white solid was filtered and discarded. The filtrate was concentrated to ca. 5 cm<sup>3</sup> and triturated with hexane, yielding an orange-red solid which was isolated by filtration. The solid was redissolved in ethyl acetate and re-precipitated with hexane to give the product as a reddish brown solid. The product was collected by filtration and dried in vacuo. Yield: 0.30 g (36%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.04 (d, I = 2.1 Hz, 2H, ArH), 6.70 (d, J = 2.1 Hz, 2H, ArH), 6.64 (s, 1H, ArH), 6.25 (d, J = 8.1 Hz, 1H, ArH), 5.97 (d, J = 8.1 Hz, 1H, ArH), 4.76 (d, J = 12.6 Hz, 2H, ArCH<sub>2</sub>), 3.82 (d, J = 12.6 Hz, 2H, ArCH<sub>2</sub>), 2.03 (s, 3H, ArCH<sub>3</sub>), 1.30 (s, 18H, <sup>t</sup>Bu), 1.21 (s, 18H, <sup>t</sup>Bu).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$  159.7, 158.1, 141.2, 136.3, 136.1, 127.8, 125.7, 125.0, 123.4, 122.5, 121.4, 115.3, 62.2, 34.8, 34.1, 31.7, 30.1, 20.6. IR (cm<sup>-1</sup>): 3426m, 2955s, 2903m, 2865m, 1607m, 1498s, 1470m, 1442m, 1414w, 1391w, 1361m, 1294s, 1253s, 1238s, 1203m, 1168m, 1128m, 1040w, 1001w, 971w, 915s v(MoO<sub>2</sub>), 891s v(MoO<sub>2</sub>), 871s, 851s, 813s, 779w, 755m, 747m, 626w, 601w, 554s, 512w, 472w. MS (ESI<sup>+</sup>): m/z 726 (25%) [M+K+H]<sup>+</sup>. Anal. Calc. for C<sub>37</sub>H<sub>50</sub>KMoNO<sub>5</sub>: C, 61.4; H, 7.0; N, 1.9. Found: C, 61.0; H, 7.2; N, 2.1%.

# 2.3.4. [vo(L<sup>2</sup>)] (**4**)

This compound was synthesised from  $[H_3L^2]$  (0.89 g, 2.0 mmol), VOCl<sub>3</sub> (0.19 cm<sup>3</sup>, 2.0 mmol), and triethylamine (0.83 cm<sup>3</sup>, 6.0 mmol) in THF (40 cm<sup>3</sup>) using a similar procedure as described above for **2**. The desired product was isolated as a dark blue solid. Yield: 0.77 g (75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.27 (d, J = 2.4 Hz, 1H, ArH), 7.20 (d, J = 1.5 Hz, 1H, ArH), 7.13 (d, J = 2.1 Hz, 1H, ArH), 6.73–6.78 (m, 2H, ArH), 6.44–6.49 (m, 3H, ArH), 6.03 (d, J = 8.1 Hz, 1H, ArH), 5.43 (d, J = 15 Hz, 1H, ArCH<sub>2</sub>), 4.81 (d, J = 15 Hz, 1H, ArCH<sub>2</sub>), 4.69 (d, J = 11.7 Hz, 1H, ArCH<sub>2</sub>), 3.46 (d, J = 11.7 Hz, 1H, ArCH<sub>2</sub>), 2.26 (s, 3H, ArCH<sub>3</sub>), 1.43 (s, 9 H, <sup>t</sup>Bu), 1.29 (s, 9H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  162.0, 159.8, 154.5, 143.8, 139.2, 134.6, 132.8, 130.2, 129.6, 128.8, 123.5, 123.0, 121.8, 121.0, 120.5, 116.4, 115.2 (one peak overlapping), 64.0 (one peak overlapping), 35.8, 35.0, 32.5, 30.2, 21.8. MS (APCI): m/z 512 (100%) [M+H]<sup>\*</sup>. Anal. Calc. for C<sub>29</sub>H<sub>34</sub>NO<sub>4</sub>V: C, 68.1; H, 6.7; N, 2.7. Found: C, 68.2; H, 6.8; N, 3.0%.

# 2.4. X-ray crystallographic analysis

Single crystals of  $[Fe(L^1)]_2$  (1) were obtained by slow evaporation of a THF solution of the complex. Crystals suitable for X-ray diffraction analysis were covered with perfluoropolyether oil, mounted on glass capillaries, and cooled rapidly to 150 K in a stream of cold N<sub>2</sub> using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf–Nonius KappaCCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Computations were performed using the SHELX-97 PC programme package on a PC computer. The structures were solved by direct phase determination and refined by full-matrix least squares with anisotropic thermal parameters for the

#### Table 1

Crystallographic data for complex  $[Fe(L^1)]_2$  (1).

Compound	$[Fe(L^1)]_2$
Molecular formula	$C_{74}H_{100}Fe_2N_2O_6$
Formula weight	1225.26
Temperature (K)	150(2)
Colour	Black needle
Crystal size (mm <sup>3</sup> )	$0.32 \times 0.08 \times 0.06$
Crystal system	triclinic
Space group	ΡĪ
a (Å)	10.2979(2)
b (Å)	11.7669(3)
c (Å)	14.2121(4)
α (°)	88.2100(10)
β (°)	83.0900(10)
γ (°)	82.1920(10)
$V(Å^3)$	1693.59(7)
Ζ	2
Density (g/cm <sup>3</sup> )	1.201
$\mu (\mathrm{mm}^{-1})$	0.480
F(000)	658
Transmission coefficients (minimum, maximum)	0.86, 0.97
Reflections collected	12127
Independent reflections $(R_{int})$	6640 (0.0358)
Observed data with $I \ge 2\sigma(I)$	5245
Number of parameters, p	408
S(GOF)	1.144
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0474$ , $wR_2 = 0.1280$
R indices (all data)	$R_1 = 0.0676, wR_2 = 0.1575$

non-hydrogen atoms [21]. Hydrogen atoms were introduced in their idealised positions and included in structure factors calculations with assigned isotropic temperature factors [22]. Selected crystallographic data for **1** are shown in Table 1.

# 3. Results and discussion

# 3.1. Synthesis of ligands

The partially unsymmetric tripodal NO<sub>3</sub> proligand  $[H_3L^1]$  was prepared according to published procedure by the reaction of 2-hydroxy-5-methylaniline and 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide in the presence of triethylamine [18]. The new fully unsymmetric proligand  $[H_3L^2]$  was synthesised by a two-step approach as outlined in Scheme 1. Treatment of 2-hydroxy-5-methylaniline with salicylaldehyde in methanol afforded the corresponding Schiff-base product as a bright orange precipitate. The latter was immediately reduced *in situ* with NaBH<sub>4</sub> to give the corresponding disubstituted amine *N*-(2-hydroxybenzyl)-*N*-(2'-hydroxy-5'-methylphenyl)amine in 97% yield. Subsequent reaction of this disubstituted amine with 3,5-di-*tert*-butyl-2-hydroxybenzylbromide in the presence of triethylamine gave proligand  $[H_3L^2]$  in 72% yield.

# 3.2. Synthesis and coordination chemistry of iron(III), oxovanadium(V) and dioxo-molybdenum(VI) complexes

The coordination chemistry of tripodal ligands  $(L^1)$  and  $(L^2)$  with vanadium, molybdenum and iron were studied in this work. Recently, we have reported on the synthesis of a mononuclear iron(III) complex derived from  $(L^1)$  [18]. This complex was prepared by the reaction of FeCl<sub>3</sub> and  $[H_3L^1]$  in the presence of triethylamine and 1-methylimidazole (Im). The solid-state structure of  $[Fe(L^1)(Im)]$  was established by X-ray crystallography. The Fe(III) centre was bound by one  $(L^1)$  ligand and one imidazole molecule, which formed a five-coordinate ligand environment around the metal centre. The imidazole nitrogen occupies the fifth coordination site in the axial position *trans* to an apical nitrogen of the tripodal ligand. The coordination chemistry of  $(L^1)$  with Fe(III) was re-examined in the



Scheme 1. Synthesis of the new fully unsymmetric N-capped tripodal NO<sub>3</sub> proligand [H<sub>3</sub>L<sup>2</sup>].

absence of imidazole and, interestingly, a dimeric complex  $[Fe(L^1)]_2$ (1) was isolated in 30% yield (Scheme 2). Fig. 2 shows the solid-state structure of 1 as determined by X-ray diffraction analysis. Selected bond lengths and angles are given in Table 2.

Compound **1** crystallises triclinic in the space group  $P\overline{1}$ . The dimeric complex is located at a crystallographic centre of inversion. The iron atoms (Fe(1) and Fe(1A)\*) are linked by two  $\mu$ -coordinated phenoxo oxygen atoms O(1) and O(1A)\*, forming a planar Fe<sub>2</sub>O<sub>2</sub> diamond core ( $\Sigma$  bond angles = 360°). The Fe–O bond distances are 2.005(1) (Fe(1)–O(1)) and 2.031(1) (Fe(1)–O(1A)), whereas the Fe(1)–O(1)–Fe(1A) and O(1)–Fe(1)–O(1A) angles are 107.34(8)° and 72.66(8)°, respectively. The Fe(1)…Fe(1A)\* distance is 3.252 Å. It is noteworthy that the two phenolate oxygens (O(1) and O(1A)\*) belong to the "ortho-substitution-free" phenolate pendants. An identical structural feature has been observed in the so-lid-state structure of a dimeric zirconium(IV) complex derived from the same ligand [19].

Each iron(III) centre in complex **1** has a five-coordinate NO<sub>4</sub> coordination environment. The coordination geometry around the iron centres can be described as distorted trigonal bipyramidal with the equatorial plane being occupied by phenolate oxygen atoms (O(1), O(2)) and O(3) for Fe(1)), whereas the two axial sites are occupied by a bridge-head nitrogen (N(1) for Fe(1)) and a bridging oxygen atom (O(1A) for Fe(1)). The observed N(1)-Fe(1)–O(1A) angle is 151.27(8)°. The iron atom is sitting slightly above the equatorial plane (ca. 0.09 Å), leaning toward the bridging phenoxo oxygen atom O(1A). The two disubstituted benzyl phenolate pendants on each (L<sup>1</sup>) ligand form two six-membered chelate rings with the metal, whilst the remaining phenolate pendant on L<sup>1</sup> forms a five-membered metallacyclic ring. The geometric features of the five-membered ring display differences with respect to those in the six-membered systems as observed previously in the closely related mononuclear iron(III) complex  $[Fe(L^1)(Im)]$  [18]. All the equatorial Fe-O and the axial Fe-N bond distances and angles observed in **1** are comparable to those in  $[Fe(L^1)(Im)]$ .

Reports on structurally characterised bis-( $\mu$ -phenoxo)-bridged diiron(III) complexes are rare. A diiron(III) complex supported by

trianionic pentadentate ligands containing a *bis*-( $\mu$ -phenoxo)bridge has been reported [23]. The Fe(III) centre in the latter complex exhibits a distorted octahedral geometry with a N<sub>2</sub>O<sub>4</sub> coordination environment. A number of Fe(III) calixarene complexes have recently been published [24] but to our knowledge, the uncommon NO<sub>4</sub> ligand environment around the iron(III) centre in a phenoxo-bridged iron(III) complex has only been reported previously in a dimeric calix[4]arene complex [25]. The Fe(III) centre in the calixarene complex exhibited a distorted trigonal pyramidal geometry with an Fe…Fe separation (3.258(2) Å) almost identical to that observed in **1**.

Reaction of  $[H_3L^1]$  with oxo-vanadium(V) trichloride in the presence of triethylamine in a THF solution afforded the corresponding oxo-vanadium(V) complex  $[VO(L^1)]$  (2) in 73% yield (Scheme 2). The <sup>1</sup>H NMR spectrum of **2** shows that the methylene protons on the (L<sup>1</sup>) ligand occur as discrete diastereotopic doublets at 4.08 and 3.92 ppm with a coupling constant of 13.5 Hz (Fig. 3). A number of oxo-vanadium(V) complexes supported by symmetric amine triphenolate ligands have been reported and found to be catalytically active towards ethylene polymerization [26].

Treatment of [MoO<sub>2</sub>(acac)<sub>2</sub>] with [H<sub>3</sub>L<sup>1</sup>] and potassium hydroxide in methanol yielded the dioxo-molybdenum(VI) complex salt  $K[MoO(L^1)]$  (3) in 36% yield (Scheme 2). The IR spectrum of the dioxo complex showed two strong absorptions at 915 and 891 cm<sup>-1</sup>, which are assignable to symmetric and asymmetric Mo=O stretches, respectively, in a *cis*-dioxo moiety [27,28]. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** are consistent with the proposed octahedral structure of the complex as shown in Scheme 2. Complex 3 possesses an internal mirror plane and upon complexation the two methylene protons on the phenolate pendants are no longer equivalent as expected: the <sup>1</sup>H NMR spectrum of **3** showed two doublets at  $\delta$  4.76 and  $\delta$  3.82 ppm with a germinal coupling constant of 12.6 Hz (Fig. 3). In fact, the <sup>1</sup>H NMR spectrum of **3** is similar to that of 2 as both complexes possess two diastereotopic methylene protons. Attempts to obtain single crystals of 3 suitable for X-ray diffraction analysis have been unsuccessful, but the solid-state structures of a number of dioxo-molybdenum(VI) complexes



Scheme 2. Synthesis of complexes 1–4 derived from unsymmetric N-capped tripodal NO<sub>3</sub> proligands  $H_3L^1$  and  $H_3L^2$ .

bound by symmetric amine triphenolate ligands have been reported [5,6].

The coordination chemistry of the fully unsymmetric proligand  $[H_3L^2]$  with VOCl<sub>3</sub> was also examined. Complex  $[VO(L^2)]$  (**4**) was obtained in 75% yield, using a similar procedure as described for **2** (Scheme 2). The <sup>1</sup>H NMR spectrum of **4** elicited four doublets signals (falling within the range of  $\delta$  5.43–3.46 ppm), which are assignable to two types of chemically inequivalent methylene groups present on the (L<sup>2</sup>) ligand. These methylene protons become diastereotopic upon complexation of (L<sup>2</sup>) to the metal

(Fig. 3). To the best of our knowledge, complex **4** is the first metal complex coordinated by an *N*-capped tripodal ligand containing three different phenolic pendant arms. Complexes **2–4** were also characterised by mass spectrometry. The APCI and ESI spectra of these complexes showed the respective  $[M+H]^+$  and  $[M+K+H]^+$  peaks.

In summary, we have reported the coordination chemistry of a partially unsymmetric N-capped tripodal NO<sub>3</sub> ligand with iron(III), oxo-vanadium(V) and dioxo-molybdenum(VI). The synthesis and characterisation of an oxo-vanadium(V) complex supported by a



**Fig. 2.** ORTEP representation (50% thermal ellipsoid) showing the molecular structure of  $[Fe(L^1)]_2(1)$  with atom labeling. Only one orientation of the twofold disordered *tert*-butyl groups is shown. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for complex  $[Fe(L^1)]_2$  (1).

$[Fe(L^1)]_2$	
Fe(1)-O(1)	2.005(1)
Fe(1)-O(1A)*	2.031(1)
Fe(1)-O(2)	1.857(1)
Fe(1)-O(3)	1.861(1)
Fe(1)-N(1)	2.204(2)
Fe(1A)*-O(1)	2.031(1)
O(1)-Fe(1)-O(1A)*	72.66(8)
O(1)-Fe(1)-O(2)	130.70(8)
$O(1A)_{*}-Fe(1)-O(2)$	102.68(8)
O(1)-Fe(1)-O(3)	115.40(8)
$O(1A)^* - Fe(1) - O(3)$	104.59(8)
O(2)-Fe(1)-O(3)	113.21(9)
O(1)-Fe(1)-N(1)	79.20(7)
$O(1A)^* - Fe(1) - N(1)$	151.27(8)
O(2)-Fe(1)-N(1)	91.22(8)
O(3)-Fe(1)-N(1)	92.42(8)
Fe(1)-O(1)-Fe(1A)*	107.34(8)

new, fully unsymmetric *N*-capped tripodal NO<sub>3</sub> ligand featuring three different phenolic arms have also been described. We believe that the various spatial requirements of each pendant arm of the totally unsymmetric environment of the ligand provides different steric environment around the metal centre. This can be considered as a plausible way for controlling routes of substrates to approach a catalytically active metal centre when a metal complex of interest is stabilised by a fully unsymmetric ligand. The fact that complex **4** is prochiral due to the intrinsic asymmetry of the ligand suggests that the vanadium complex as formed is racemic but it might be possible to resolve the enantiomers using a suitable chiral column. It would have to be seen if the asymmetry at the metal reaction site is sufficient to orientate the substrate appropriately to give an excess of one isomer. We envisage possible applications with the new tripodal ligand in obtaining asymmetric catalysts.



**Fig. 3.** <sup>1</sup>H NMR spectra (300 MHz,  $CDCl_3$ ) of (a) oxo-vanadium(V) complex **2**, (b) dioxo-molybdenum(VI) complex **3** and (c) oxo-vanadium(V) complex **4**.

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# Appendix A. Supplementary material

CCDC 808981 contains the supplementary crystallographic data for for  $[Fe(L^1)]_2$  (1). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2011.10.054.

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