

Synthesis and structure of iron(III) complexes of amine-bis(phenolate) ligands

Elliott F. Chard, John R. Thompson, Louise N. Dawe, and Christopher M. Kozak

Abstract: The synthesis and structures of four new iron(III) amine-bis(phenolate) complexes are reported. Reaction of anhydrous FeCl₃ with the diprotonated tridentate ligand isopropyl-N,N-bis(2-methylene-4-t-butyl-6-methylphenol) (H₂L1) and NEt₃ produces the trigonal bipyramidal iron(III) complex [NEt₃H]⁺ [FeCl₂L1]⁻ (1). The reaction of FeBr₃ with the sodium or lithium salts, Na₂L1 and Li₂L2, results in the formation of FeBr₂L1H (2) and FeBr₂L2H (3), tetrahedral iron(III) complexes possessing two bromide ligands and quaternized ammonium fragments. A trigonal bipyramidal Fe^{III} hydroxido-bridged dimer, [Fe(μ -OH)L2]₂ (4), was also isolated during the synthesis of 3. Single-crystal X-ray molecular structures have been determined for complexes 1–4 and H₂L2.

Key words: iron, amine-bis(phenolate), crystallography, ligand design, coordination chemistry.

Résumé : La synthèse et les structures de quatre nouveaux complexes de fer(III) et d'amine-bis(phénolate) sont décrites. La réaction du FeCl₃ anhydre avec le ligand tridendate diprotoné l'isopropyl-N,N-bis(2–methylène-4-*t*-butyl-6-méthylphénol) (H₂L1) et le composé NEt₃ produit le complexe de fer(III) trigonal bipyramidal [NEt₃H]+[FeCl₂L1]⁻ (1). La réaction du FeBr₃ avec les sels de sodium ou de lithium, Na₂L1 et Li₂L2, conduit à la formation des composés FeBr₂L1H (2) et FeBr₂L2H (3), complexes de fer(III) tétraédriques qui possèdent deux ligands bromures et des fragments d'ammonium quaternaire. Un dimère de fer(III) trigonal bipyramidal avec pont hydroxyde, [Fe(μ -OH)L2]₂ (4), a également été isolé au cours de la synthèse du composé 3. Les structures moléculaires des complexes 1 à 4 et du complexe H₂L2 ont été déterminées par cristallographie aux rayons X. [Traduit par la Rédaction]

Mots-clés : fer, amine-bis(phénolate), cristallographie, conception de ligands, chimie de la coordination.

Introduction

Recently, the use of chelating amine-bis(phenolates) as ligands has played a very important role in transition metal catalyst design. These dianionic ligands are extremely diverse and have been used primarily with high-valent early transition metals for which the "hard" acid and base properties are well matched.¹ Numerous Fe^{III} complexes supported by these ligands have been investigated,^{2–23} many of them as a result of their close relationship with phenol-containing ligands found in non-heme-iron-containing metalloenzymes.

We are interested in the development of new inexpensive ironbased catalysts for organic synthesis. Previously, we reported the catalytic potential of iron complexes supported by various tridentate and tetradentate amine-bis(phenolate) ligands (Fig. 1).^{24–31} For example, we have investigated the cross-coupling of aromatic Grignard reagents with alkyl halides using iron(III) catalysts bearing amine-bis(phenolate) ligands.^{24,26–28,31} In an attempt to generate more reactive catalysts while still maintaining the robust nature of the catalyst precursor, we turned our attention to tridentate amine-bis(phenolate) ligands. However, the reduced coordination ability and ligand field strength of these tridentate variations can lead to a number of unexpected products upon metallation.

These ligand precursors can be coordinated to transition metals by several routes. For example, alkali metal compounds of these ligands can be first prepared using *n*-BuLi or NaH to generate M_2L salts where M = Li or Na, respectively. Salt metathesis of transition metal halides with these M_2L compounds generates the desired transition metal amine-bis(phenolate) complexes. Several structurally characterized examples of alkali metal compounds of aminebis(phenolate) compounds have recently been reported,32-43 A protonolysis route may also be employed for labile transition metal halides. For example, FeCl3 reacts with amine-bis(phenolate) ligands in the presence of NEt₃ resulting in complexes of the formula FeCIL. This gives compounds that are monomeric in the solid state when tetradentate ligands are used^{24,25,30} but leads to dimeric structures for tridentate ligands.²⁷ The dimeric complexes exist as halide-bridged species possessing distorted trigonal bipyramidal iron(III) ions. If bulky groups such a *t*-pentyl substituents are present on the phenolate donors, then monomeric Fe^{III} compounds may also be obtained using tridentate ligands.³¹ These previous tridentate amine-bis(phenolate) ligands contained benzyl or n-propyl amine groups. However, we found that other Fe^{III} complexes could be generated depending on the nature of the halide ligands present, the purification procedures used, and the steric requirements of the amine-bis(phenolate) backbone. Herein we report the synthesis and structure of four new structurally authenticated iron(III) complexes supported by tridentate amine-bis(phenolate) ligands.

Results and discussion

The tridentate amine-bis(phenol) ligand precursors H_2L1 and H_2L2 (Fig. 1) were readily synthesized by a modified Mannich condensation reaction in which the 2,4-disubstituted phenol, amine, and formaldehyde were heated to reflux in water for 12 h. Single crystals of H_2L2 suitable for X-ray diffraction were obtained from

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онно онно R' R 'n" Ŕ" R, R' = t-Bu, Me, t-Pentyl R, R' = t-Bu, Me, t-Pentyl, Cl R" = n-Pr, Bn ∠NMe₂ t-Bu t-Bu t-Bu t-Bu онно онно t-Bu -Bu Me Me H_2L1 H₂L2

Fig. 1. Proligands previously used with Fe^{III} by the authors and

those used in this study (H₂L1 and H₂L2).

a saturated methanol solution at -20 °C. The solid-state molecular structure and the crystallographic data of H₂L2 can be found in Fig. 2 and Table 1, respectively. Bond lengths and angles can be found in the supplementary data (see "Supplementary material" section).

The reaction of FeCl₃ with H₂L1 followed by addition of NEt₃ to sequester the HCl produced (Scheme 1) was expected to yield a compound formulated as FeClL, as was observed in previous work from our group involving the *n*-propylamino-containing ligand. Instead, the solid-state molecular structure of 1 (shown in Fig. 3) reveals a trigonal bipyramidal iron(III) centre with a formal negative charge (hence, an "ate" complex) and a triethylammonium counterion. Elemental analysis performed on a recrystallized sample of 1 confirms this formulation for the bulk sample. ¹H NMR spectroscopy revealed only broad and inconclusively assignable peaks due to the paramagnetism of the compound. Indeed, no clearly assignable peaks were observed in the ¹H NMR spectra of any of the Fe^{III} compounds reported herein. Selected bond lengths and angles for compound 1 (as well as for 2 and 3) are given in Table 2. The equatorial plane of the Fe^{III} ion in 1 consists of two phenolate oxygens, O(1) and O(2), and a chloride ion, Cl(2), where the sum of bond angles is 359.69°, indicating near perfect planarity. The iron atom is displaced 0.06 Å above the equatorial plane. The amine nitrogen donor N(1) and the chloride ion Cl(1) occupy the apical sites, giving a Cl(1)–Fe(1)–N(1) bond angle of 178.85(7)°, which is close to the ideal linear geometry. The cis-oriented chloride ligands are nearly orthogonal with a Cl(1)-Fe(1)-Cl(2) bond angle of 91.42(5)°. The distorted trigonal bipyramidal coordination environment of the Fe^{III} ion possesses a trigonality index parameter, τ , value of 0.837 as defined by Addison and Reedijk.⁴⁴ $\tau = (\beta - \alpha)/60$, where β represents the largest angle about the metal centre and α represents the second largest angle about the metal centre. For perfect trigonal bipyramidal and square pyramidal geometries, the τ values are 1.0 and 0, respectively.

Previously, we reported mononuclear trigonal bipyramidal iron(III) complexes of related tetradentate diamine-bis(phenolate) ligands (abbreviated $[O_2NN']$, where N' represents a pendant dimethyl-aminoethyl, $[O_2NN']^{NMe2}$, or pyridyl, $[O_2NN']^{Py}$, arm).³⁸ The Fe–Cl bond lengths in FeCl $[O_2NN']^{Py}$ and FeCl $[O_2NN']^{NMe2}$ were found to be 2.3051(10) and 2.2894(5) Å respectively, which are very similar to the Fe(1)–Cl(2) interaction observed in the equatorial plane of **1**. The Fe(1)–Cl(1) bond length (2.3618(13) Å) in **1**, where Cl(1) is *trans* to a nitrogen donor, is slightly longer than the Fe–Cl bond lengths observed in FeCl $[O_2NN']^{Py}$ and FeCl $[O_2NN']^{NMe2}$ (where Cl is also *trans* to an amino nitrogen donor). **1** has a Fe(1)–N(1) distance of 2.255(3) Å, which is

Fig. 2. Single-crystal X-ray structure of H_2 **L2**. Hydrogen atoms (except those on O(1) and O(2)) omitted for clarity. Ellipsoids are shown at 50% probability. Bond lengths and angles are given in the supplementary data.



very similar to the Fe–N bond lengths reported in FeCl[O₂NN']^{Py} (2.2706(15) Å) and FeCl[O₂NN']^{NMe2} (2.248(2) Å). The phenolate oxygen atoms in **1** exhibit bond distances of 1.855(2) and 1.848(2) Å for Fe(1)–O(1) and Fe(1)–O(2), respectively. These interactions are only slightly shorter than those observed in the FeCl[O₂NN'] complexes where average Fe–O distances of 1.86 Å are observed.

The coordination geometry around iron(III) in 1 is very closely related to a pair of iron(III) chloride-bridged dimers bearing *n*-propyl and benzyl amines, [Fe(µ-Cl)[ONO]^{nPr}]₂ (A) and [Fe(µ-Cl)[ONO]^{Bn}]₂ (B), previously reported in our group.²⁷ Like 1, the five-coordinate trigonal bipyramidal iron(III) centres in A and B are composed of two chloride ions along with two phenolate oxygen donor atoms and a central amine nitrogen atom originating from a tridentate amine-bis(phenolate) backbone. The axial Fe-Cl bond length in 1 (2.3618(4) Å) is slightly shorter than the axial Fe-Cl bond lengths found in A (2.4911(8) Å) and B (2.5025(3) Å). The equatorial Fe(1)–Cl(2) bond length in 1 (2.3038(14) Å) is intermediate to the equatorial Fe–Cl bond lengths reported in A (2.298(2) Å) and B (2.3290(4) Å). The Fe(1)-N(1) distance of 2.255(3) Å observed in 1 is longer than the observed Fe-N distances found in both chloride-bridged dimers of 2.183(4) Å in A and 1.1819(10) Å in B. The Fe-O distances in 1 are 1.855(2) and 1.848(3) Å for Fe(1)-O(1) and Fe(1)–O(2), respectively, which are longer than the distances reported between iron and the phenolate oxygen atoms in A (average distance of 1.818 Å) and **B** (average distance of 1.825 Å). Since the iron centre in 1 has a formal negative charge, the anionic oxygen donors may be slightly repelled by the metal centre. From an electronic perspective, this may account for the longer Fe-O distances observed in 1. Of course, in the case of both A and B, steric hindrance originating from the presence of two large amine-bis(phenolate) ligands about the two iron(III) centres may also be a major contributor. The amine nitrogen donor and a bridging chloride ion take up the axial positions, giving a Cl(1)*-Fe(1)-N(1) bond angle of 178.32(9)° in A and a Cl(2)-Fe(1)-N(1) bond angle of 177.28(3)° in B. Complex 1 has a Cl(1)-Fe(1)-N(1) bond angle of 178.85(7)°, which is closer to the ideal linear geometry. The cis-oriented chloride ligands are nearly orthogonal with a Cl--Fe-Cl bond angle of 87.36(4)° in A and 84.341(14)° in B. The Cl⁻-Fe-Cl bond angle in 1 is 91.42(5)°, which is closer to the perfect orthogonal angle of 90°.

In 2002, Leznoff and co-workers reported a five-coordinate iron(III) chloride-bridged dimer with a distorted trigonal bipyramidal geometry.⁴⁵ Unlike the coordination environment of **1**, which contains two anionic oxygen donor atoms and a central

Compound	H ₂ L2	1	2	3	4
Chemical formula	C33H23NO2	C ₃₃ H ₅₅ Cl ₂ FeN ₂ O ₂ ·C ₇ H ₈	$C_{27}H_{40}Br_{2}FeNO_{2}\cdot 2.5(C_{7}H_{8})$	C ₃₃ H ₅₂ Br ₂ FeNO ₂ ·C ₇ H ₈	$C_{66}H_{104}Fe_2N_2O_6\cdot 2(C_7H_8)$
Colour	Colourless	Dark red	Black	Dark red	Red
Habit	Prism	Prism	Prism	Prism	Prism
Formula mass	496.76	730.70	856.62	802.57	1317.53
Crystal system	Mononclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic
a (Å)	15.185(4)	11.162(3)	14.816(4)	10.5127(10)	24.3216(17)
b (Å)	11.707(3)	11.397(4)	16.729(4)	13.6960(14)	18.1938(11)
c (Å)	18.596(4)	17.686(6)	18.202(5)	15.3413(15)	18.8654(12)
α (°)	90	83.003(14)	90	68.421(5)	90
β (°)	108.298(4)	75.944(13)	107.386(3)	79.693(6)	90
γ (°)	90	69.005(11)	90	77.951(6)	90
Unit cell V (Å ³)	3138.7(12)	2036.1(11)	4305.4(20)	1996.1(3)	8348.0(9)
Temperature (K)	158(1)	163(1)	163(1)	163(1)	193(1)
Space group	P2 ₁ /c (#14)	P-1 (#2)	$P2_1/c$ (#14)	P-1 (#2)	Pccn (#56)
Ζ	4	2	4	2	4
$D_{\rm c}$ (g/cm ³)	1.049	1.192	1.321	1.335	1.048
Radiation type	ΜοΚα	ΜοΚα	ΜοΚα	ΜοΚα	ΜοΚα
Absorption, μ (mm ⁻¹)	0.630	0.535	2.246	2.412	0.393
F(000)	1096	786	1784	838	2856
Reflections measured	40638	17721	54221	14400	24717
Independent reflections	6483	8338	8910	6952	5448
R _{int}	0.0369	0.0574	0.0588	0.0962	0.1590
R_1 (all)	0.0880	0.0902	0.0701	0.1683	0.2272
$wR(F_2)$ (all)	0.2384	0.1905	0.1483	0.2578	0.4243
$R_1 (I > 2\sigma(I))^a$	0.0830	0.0634	0.0565	0.0991	0.1586
$wR(F^2)$ $(I > 2\sigma(I))^b$	0.2337	0.1577	0.1386	0.2159	0.3791
Goodness of fit on F ²	1.157	1.093	1.104	1.035	1.177
CCDC reference	982453	982454	982455	982456	982457

Table 1. Crystallographic and structure refinement data for H₂L2 and 1–4.

 ${^aR_1} = \Sigma \; (|F_{\rm o}| - |F_{\rm c}|) / \Sigma |F_{\rm o}|). \label{eq:R1}$

 ${}^{b}wR_{2} = [\Sigma (w(F_{o}^{2} - F_{c}^{2})^{2})/\Sigma w(F_{o}^{2})^{2}]^{1/2}.$

Scheme 1. Synthesis of 1.



Fig. 3. Molecular structure (ORTEP) and partial atom labeling of **1**. Hydrogen atoms (except at N(2)) and cocrystallized solvent molecules omitted for clarity. Ellipsoids are shown at 50% probability.



Table 2. Selected bond lengths (Å) and bond angles (°) of 1–3.

	1	2	3
Fe(1)–O(1)	1.855 (2)	1.822 (2)	1.843 (6)
Fe(1)–O(2)	1.848 (3)	1.832 (3)	1.851 (6)
Fe(1)–X(1) ^a	2.3618 (13)	2.3596 (9)	2.355 (2)
Fe(1)–X(2)	2.3038 (14)	2.3491 (8)	2.3697 (19)
Fe(1)–N(1)	2.255 (3)		
Fe(1)…N(1)		3.439 (4)	3.429 (7)
O(1)-Fe(1)-O(2)	114.58 (12)	106.38 (13)	105.9 (3)
O(1)-Fe(1)-X(1)	91.49 (8)	108.43 (8)	108.9 (2)
O(1)-Fe(1)-X(2)	128.60 (10)	110.90 (9)	110.8 (2)
O(2)-Fe(1)-X(1)	92.71 (9)	110.71 (9)	107.5 (3)
O(2)-Fe(1)-X(2)	116.51 (8)	110.08 (9)	112.0 (2)
X(1)–Fe(1)–X(2)	91.42 (5)	110.26 (3)	111.53 (7)
Cl(1)-Fe(1)-N(1)	178.85 (7)		
Cl(2)-Fe(1)-N(1)	89.35 (9)		
O(1)-Fe(1)-N(1)	87.35 (10)		
O(2)-Fe(1)-N(1)	87.71 (11)		

 $^{a}X = Cl$ for compound 1 and Br for compounds 2 and 3.

nitrogen donor, the iron(III) centre in {Fe(μ -Cl)[^tBuN(SiMe₂)]₂O}₂ is composed of two anionic nitrogen donor atoms and a neutral central oxygen donor. The Fe–Cl bond lengths in {Fe(μ -Cl)[^tBuN(SiMe₂)]₂O}₂ are 2.3181(19) and 2.4652(17) Å whereas the corresponding distances in **1** are 2.3618(14) and 2.3038(14) Å. The Cl–Fe–Cl bond angle in {FeCl[^tBuN(SiMe₂)]₂O}₂ is 86.75(6)°, which is lower than the Cl–Fe–Cl angle observed in **1** (91.42(5)°) and intermediate to those observed in **A** (87.36(6)°) and **B** (84.341(14)°).

When the sodium and lithium salts prepared from the reaction of NaH with H₂L1 and *n*-BuLi with H₂L2 in THF at -78 °C were reacted with anhydrous FeBr₃, zwitterionic tetrahedral iron(III) complexes 2 and 3 bearing two bromide ligands and quaternized ammonium fragments were generated (Scheme 2). A similar complex was previously reported by us using NEt₃ as the base.²⁷ The Scheme 2. Synthesis of 2-4.



mass spectra of **2** and **3** show peaks corresponding to the loss of one bromide ligand from the parent ion along with the proton of the central nitrogen atom ($[M-Br]^+$). There also exist peaks corresponding to the loss of both bromide ligands and the proton of the central nitrogen atom ($[M-2Br]^+$) from the parent ion.

Single crystals of 2 and 3 suitable for X-ray diffraction were obtained from saturated toluene solutions at -35 °C inside a nitrogen-filled glove box. The solid-state molecular structures of 2 and 3 are shown in Fig. 4. In the solid state, complexes 2 and 3 exhibit monomeric structures having tetrahedral iron(III) centres. Unlike complex 1, and also unlike the previously reported iron(III) complexes of amine-bis(phenolate) ligands,²⁷ the bis(phenolate) ligands in 2 and 3 bind in a bidentate fashion. The central nitrogen donors in 2 and 3 are protonated, giving quaternized ammonium groups. The oxygen donors of the phenolate groups remain anionic, giving net monoanionic ammonium-bis(phenolate) ligands. Two bromide ions and the phenolate oxygen donor atoms make up the tetrahedral coordination environment about the iron(III) centres in 2 and 3. The four-coordinate tetrahedral iron(III) centres are thereby formally anionic, resulting in zwitterionic iron(III) complexes. The bond angles around the metals range from 106.38 (13)° to 110.90(9)° in 2 and from 105.9(3)° to 112.0(2)° in 3, which are only moderately distorted from the ideal tetrahedral angle of 109.5°. The bond lengths of Fe(1)-Br(1) and Fe(1)-Br(2) are slightly asymmetrical in 2 and 3. The Fe-Br distances in 2 are 2.3596(9) and 2.3491(8) Å for Fe(1)-Br(1) and Fe(1)-Br(2), respectively, while the Fe-Br distances in 3 are 2.355(2) and 2.3697(19) Å for Fe(1)-Br(1) and Fe(1)-Br(2), respectively. The Fe-Br distances observed in 2 and 3 are similar to the terminally bonded Fe-Br bond length (2.3683(11) Å) found in a previously reported mononuclear square pyramidal iron(III) bromide complex (FeBr[O2N2]) containing a salan ligand.²⁵ In 2, the phenolate oxygen atoms exhibit bond distances to iron of 1.822(2) and 1.832(3) Å for Fe(1)-O(1) and Fe(1)-O(2), respectively. The Fe(1)-O(1) and Fe(1)-O(2) bond lengths observed in the related complex 3 (containing bulkier 2,4-di-t-butylphenolate groups) are slightly longer, with distances of 1.843(6) and 1.851(6) Å, respectively. The Fe-O interactions observed in 2 and 3 are similar to those observed in FeBr[O₂N₂], where average Fe–O distances of 1.837 Å are observed.²⁵

Fig. 4. Molecular structures (ORTEP) and partial atom labeling of **2** (top) and **3** (bottom). Hydrogen atoms (except for H(1)) and cocrystallized solvent molecules omitted for clarity. Ellipsoids are shown at 50% probability.



The coordination geometries of 2 and 3 are similar to a tetrahedral iron(III) complex that we previously reported, abbreviated FeBr₂[O₂NH]^{BuMenPr}.²⁷ Like **2**, FeBr₂[O₂NH]^{BuMenPr} contains 2-t-butyl-4methylphenolate groups. However, unlike 2 and 3, which possess isopropyl alkyl groups on the central nitrogen donors, the nitrogen donor of FeBr₂[O₂NH]^{BuMenPr} contains a *n*-propyl alkyl substituent. The Fe-O bond lengths of 1.828 (3) and 1.836 (3) Å observed in FeBr₂[O₂NH]^{BuMenPr} are slightly shorter than the corresponding Fe-O distances found in 3. However, the Fe-O bond lengths are very similar to those observed in 2. Similarly, as found in both 2 and 3, the Fe–Br bond lengths observed in FeBr₂[O₂NH]^{BuMenPr} are slightly asymmetrical. The Fe(1)-Br(2) bond length (2.3723(7) Å) observed in FeBr₂[O₂NH]^{BuMenPr} is slightly longer than the Fe–Br distances found in 2 and 3. The bond angles around the iron centre range from 105.24(15)° to 112.87(10)° in $\text{FeBr}_2[O_2\text{NH}]^{Bu\text{MenPr}}$ and from 106.38(13)° to 110.90(9)° in 2. Since both complexes share the same substituents on the phenolate rings, the differences in bond angles observed may be attributed to the differences in sterics originating from the alkyl substituents on the central nitrogen donor.

During the preparation of **3**, crystals were obtained that upon diffraction revealed that a second species was formed. The structure is shown in Fig. 5 and selected bond lengths and angles are given in Table 3. Complex **4** was isolated in good yield instead of the expected iron bromide compound. As reported by Attia and **Fig. 5.** Molecular structure (ORTEP) and partial atom labeling of **4**. Hydrogen atoms (except for H(1)), *t*-butyl methyl groups, and cocrystallized toluene molecules omitted for clarity. Ellipsoids are shown at 50% probability. Symmetry operations used to generate equivalent atoms (asterisks): -x + 1, -y + 1, -z.



Table 3. Selected bond lengths (Å) and bond angles (°) of 4.

Fe(1)–Fe(1) ^a	3.13645 (17)	Fe(1)-O(1)	1.857 (8)
Fe(1)-O(2)	1.870 (8)	Fe(1)-O(3)	1.980 (8)
Fe(1)-O(3)a	2.010 (8)	Fe(1)-N(1)	2.214 (10)
Fe(1)a-Fe(1)-O(1)	106.8 (2)	Fe(1)a-Fe(1)-O(2)	117.8 (2)
Fe(1)a-Fe(1)-O(3)	38.5 (2)	Fe(1)a-Fe(1)-O(3)a	37.9 (2)
Fe(1)a-Fe(1)-N(1)	133.3 (2)	O(1)-Fe(1)-O(2)	116.9 (4)
O(1)-Fe(1)-O(3)	110.2 (4)	O(1)-Fe(1)-O(3) ^a	96.4 (3)
O(1)-Fe(1)-N(1)	91.4 (3)	O(2)-Fe(1)-O(3)	132.6 (4)
O(2)-Fe(1)-O(3)a	93.5 (3)	O(2)-Fe(1)-N(1)	88.6 (3)
O(3)-Fe(1)-O(3) ^a	76.38 (5)	O(3)-Fe(1)-N(1)	95.0 (3)

aSymmetry operations used to generate equivalent atoms: -x + 1, -y + 1, -z.

co-workers, treatment of a monomeric Fe^{III} species (with coordinated monoanionic ligands) with a strong base (such as KOH) at room temperature leads to a μ -dihydroxido Fe^{III} species.⁴⁶ If LiOH was present as an impurity in the *n*-BuLi used for the reaction, it may have led to formation of the observed hydroxido-bridged dimer. Indeed, when the reaction is repeated with freshly obtained and titrated *n*-BuLi, compound **3** is exclusively obtained. In the mass spectrum of **4**, a molecular ion peak ([M]+) is evident. An intense [M–OH]+ peak was also observed in the mass spectrum.

The data obtained from single crystals of **4** were consistently of poor quality and led to very weak diffraction at high angles (low cutoff in 20 (45°)); however, we include the results for connectivity purposes.⁴⁷ In the solid state, **4** exhibits a dimeric structure resulting in trigonal bipyramidal iron(III) centres bridged by hydroxide ligands. A similar compound ([Fe(μ -OH)[ONO]^{BuMeMe}]₂) has been previously reported by Chaudhuri and co-workers.⁴⁸ However, unlike **4**, which contains 2,4-di-t-butylphenolate groups, [Fe(μ -OH)[ONO]^{BuMeMe}]₂ possesses 2-t-butyl-4-methylphenolate groups, which may impart more of an electronic rather than a steric difference at the metal centre. Perhaps more significant is that the central nitrogen donor of [Fe(μ -OH)[ONO]^{BuMeMe}]₂ contains a meth-yl substituent, while the central nitrogen donor in **4** possesses a bulkier isopropyl group. Like [Fe(μ -OH)[ONO]^{BuMeMe}]₂, two phe-

nolate oxygen donor atoms and a bridging hydroxido oxygen atom occupy the equatorial plane around each iron ion in **4**. The amine nitrogen and the bridging hydroxido oxygen atom O(3)* take up the axial positions in **4** and $[Fe(\mu-OH)[ONO]^{BuMeMe}]_2$. The O (3)*-Fe(1)-N(1) bond angles in **4** and $[Fe(\mu-OH)[ONO]^{BuMeMe}]_2$ are considerably distorted from the ideal linear geometry.

Conclusions

A series of iron(III) complexes supported by amine-bis(phenolate) ligands has been prepared. Complex 1 exhibits mildly distorted trigonal bipyramidal coordination geometry whereas 2 and 3 contain distorted tetrahedral Fe^{III} centres. Unlike complexes 1–3, complex 4 was determined to be dimeric in the solid state, giving distorted trigonal bipyramidal iron(III) ions bridged by hydroxido ligands. The central nitrogen donors of 2 and 3 are protonated to give a quaternized ammonium fragment. Complexes 1–4 and ligand H₂L2 have been structurally characterized by single-crystal X-ray diffraction. Additionally, all paramagnetic Fe^{III} complexes have been analytically verified by elemental analysis and MALDI-TOF mass spectrometry. Ligand precursors H₂L1 and H₂L2 have been characterized by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectrometry (HRMS).

Experimental

General methods and materials

All iron complexes were synthesized under an atmosphere of dry nitrogen by means of standard Schlenk techniques or by using an MBraun LabmasterDP glove box. THF was stored over 4 Å molecular sieves and distilled from sodium benzophenone ketyl under nitrogen. Anhydrous toluene was purified using an MBraun solvent purification system. Anhydrous FeCl₃ (97%) and FeBr₃ (99%) were obtained from Strem Chemicals. Other reagents were purchased from Strem, Sigma-Aldrich, or Alfa Aesar and used without further purification.

NMR spectra were recorded using CDCl₃ solutions on a Bruker Avance III 300 MHz instrument with a 5 mm multinuclear broadband observe (BBFO) probe. MALDI-TOF MS spectra were performed using an ABI QSTAR XL Applied Biosystems/MDS hybrid quadrupole TOF MS/MS system equipped with an oMALDI-2 ion source. Samples were prepared at a concentration of 10.0 mg/mL in toluene. Anthracene was used as the matrix, which was mixed at a concentration of 10.0 mg/mL. Infrared spectra were recorded on a Bruker Alpha FTIR spectrometer equipped with diamond ATR sampling. HRMS spectra were recorded using a High Resolution MSD Waters Micromass GCT Premier spectrometer equipped with an electron impact ion source and a time-of-flight (TOF) mass analyzer. Melting point data were collected on a MPA100 OptiMelt automated melting point system. Elemental analyses were carried out by Canadian Micro-analytical Services Ltd., Delta, British Columbia.

Crystallographic data were solved on an AFC8-Saturn 70 single crystal X-ray diffractometer from Rigaku/MSC, equipped with an X-stream 2000 low-temperature system and a SHINE optic. The data were processed using CrystalClear⁴⁷ software and corrected for Lorentz and polarization effects and absorption.48 Neutral atom-scattering factors for all nonhydrogen atoms were taken from the "International Tables for X-ray Crystallography".⁴⁹ The structures were solved by direct methods using SIR92⁵⁰ and expanded using Fourier techniques (DIRDIF99).⁵¹ All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Anomalous dispersion effects were included in F_{calc} ;⁵² the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁵³ The values for the mass attenuation coefficients are those of Creagh and Hubbell.54 All calculations were performed using the CrystalStructure⁵⁵ crystallographic software package except for refinement, which was performed using SHELXL-97.⁵⁶ Structural illustrations were created using ORTEP-III (v. 2013.1) for Windows.⁵⁷

H₂[O₂N]^{BuMeiPr} (H₂L1)

To a stirred mixture of 2-t-butyl-4-methylphenol (20.398 g, 0.1232 mol) in 100 mL of deionized water was added 37% aqueous formaldehyde (10 mL, 0.1232 mol) followed by slow addition of isopropylamine (3.55 g, 0.0615 mol). The reaction was heated to reflux for 12 h. Upon cooling, the reaction mixture separated into two phases. The upper phase was decanted and the remaining oily residue was triturated with cold methanol to give an analytically pure, white powder (16.25 g, 64%); mp range 130.2–131.7 °C. ¹H NMR (300 MHz, CDCl₃) δ : 7.00 (s, ArH, 2H), 6.73 (s, ArH, 2H), 3.65 (s, CH₂, 4H), 3.16 (septet,³J = 5 Hz, CH, 1H), 2.24 (s, CH₃, 6H), 1.39 (s, CDCl₃) δ : 152.68 (Ar), 136.80 (Ar), 128.93 (Ar), 128.03 (Ar), 127.20 (Ar), 122.36 (Ar), 51.64 (CH₂), 48.33 (CH), 34.59 (C(CH₃)₃), 29.64 (C(CH₃)₃), 20.80 (ArCH₃), 16.64 (CH(CH₃)₂). HRMS (TOF MS EI+): *m/z* [M]⁺ calcd. for H₂L1: 411.3137; found: 411.3143.

H₂[O₂N]^{BuBuiPr} (H₂L2)

To a stirred mixture of 2,4-di-t-butylphenol (26.491 g, 0.1232 mol) in 100 mL of deionized water was added 37% aqueous formaldehyde (10 mL, 0.1232 mol) followed by slow addition of isopropylamine (3.55 g, 0.0615 mol). The reaction was heated to reflux for 12 h. Upon cooling, the reaction mixture separated into two phases. The upper phase was decanted and the remaining light orange solid was triturated with cold methanol to give an analytically pure, white powder (17.32 g, 57%); mp range 142.5-143.3 °C. 1H NMR (300 MHz, CDCl₃) & 7.21 (s, ArH, 2H), 6.92 (s, ArH, 2H), 3.71 (s, CH₂, 4H), 3.17 (septet, ³J = 5 Hz, CH, 1H), 1.39 (s, CH₃, 18H), 1.28 (s, CH₃, 18H), 1.18 (d,³J = 5 Hz, CH₃, 6H). ¹³C{¹H} NMR (300 MHz, 298 K, CDCl₃) δ: 152.60 (ArCOH), 141.43 (Ar), 136.02 (Ar), 125.03 (Ar), 123.41 (Ar), 121.63 (Ar), 52.00 (NCH(CH₃)₂), 48.40 (ArCH₂), 34.88 (C(CH₃)₃), 34.18 (C(CH₃)₃), 31.67 (C(CH₃)₃), 29.70 (C(CH₃)₃), 16.66 (CH(CH₃)₂). HRMS (TOF MS EI+): *m*/*z* [M]⁺ calcd. for H₂L2: 495.4076; found: 495.4063. IR (neat) v: 3196, 2958, 2905, 2865, 1606, 1476, 1451, 1391, 1362, 1290, 1225, 1207, 1157, 1123, 1078, 1027, 995, 967, 935, 879, 824, 792, 755, 722, 682, 653, 600, 540, 503 cm⁻¹.

[NEt₃H] + [FeCl₂L1]⁻ (1)

To a THF solution (50 mL) of recrystallized H_2L1 (2.00 g, 4.87 mmol) was added a solution of anhydrous FeCl₃ (0.800 g, 4.93 mmol) in THF resulting in an intense purple solution. To this solution was added triethylamine (1.00 g, 9.86 mmol) and the resulting mixture was stirred for 2 h. After stirring, the dark purple solution was filtered through Celite. Removal of solvent under vacuum yielded a dark purple solid. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution (1.693 g, 55%). Anal. calcd. for $C_{33}H_{55}Cl_2FeN_2O_2 \cdot (C_7H_8)_{1.3}$: C 66.68, H 8.69, N 3.69; found: C 66.73, H 8.92, N 3.44.

FeBr₂L1H (2)

A THF solution (50 mL) of recrystallized H_2L1 (2.00 g, 4.86 mmol) was added dropwise to a NaH suspension (0.467 g, 19.45 mmol) in THF at -78 °C. Upon warming to room temperature, the sodium salt of the ligand was added dropwise to a THF solution of anhydrous FeBr₃ (1.44 g, 4.86 mmol) at -78 °C resulting in an intense purple solution. After stirring for 2 h, the solvent was removed via vacuum to give a dark purple powder. The dark purple solid was then extracted with minimal toluene and the resulting dark purple solution was filtered through Celite. The solution was then placed in a freezer at -35 °C for recrystallization whereupon dark purple crystals suitable for X-ray diffraction were obtained (1.958 g, 64%). Anal. calcd. for C₂₇H₄₀Br₂FeNO₂: C 51.78, H 6.44, N 2.24; found: C 51.53, H 6.18, N 2.07. MALDI-TOF *m*/*z* (%, ion): 412.296 (100, [M–Fe–2Br]⁺), 465.215 (7, [M–2Br]⁺), 545.135 (3, [M–Br]⁺).

FeBr₂L2H (3)

A 1.6 mol/L hexane solution of *n*-butyllithium (5.50 mL, 8.87 mmol) was added via syringe to a stirred solution of H_2L2 (2.00 g, 4.03 mmol) in THF (50 mL) at -78 °C. Upon return to room temperature, the lithiated ligand (clear pale yellow solution) was transferred via cannula to a solution of anhydrous FeBr₃ (1.19 g, 4.03 mmol) in THF (30 mL) at -78 °C. After stirring for 2 h, the solvent was removed via vacuum to give a dark purple powder. The dark purple solid was then extracted with minimal toluene and the resulting dark purple solution was filtered through Celite. The solution was then placed in a freezer at -35 °C for recrystallization whereupon dark red crystals suitable for X-ray diffraction were obtained (2.156 g, 76%). Anal. calcd. for $C_{33}H_{52}Br_2FeNO_2$: C 55.79, H 7.38, N 1.97; found: C 55.61, H 7.19, N, 2.11. MALDI-TOF *m*/*z* (%, ion): 710.468 (2, [M]⁺), 549.260 (10, [M-2Br]⁺), 492.320 (100, [M-Fe-2Br]⁺).

$[Fe(\mu-OH)L2]_{2}$ (4)

The reaction was performed as for the synthesis of 3; however, upon recrystallization, compound 4 was obtained due to the presence of hydroxide (see "Results and discussion" section). A 1.6 mol/L hexane solution of *n*-butyllithium (5.50 mL, 8.87 mmol) was added via syringe to a stirred solution of H₂L2 (2.00 g, 4. 03 mmol) in THF (50 mL) at -78 °C. Upon return to room temperature, the lithiated ligand (clear pale yellow solution) was transferred via cannula to a solution of anhydrous FeBr₃ (1.19 g, 4.03 mmol) in THF (30 mL) at -78 °C. After stirring for 2 h, the solvent was removed via vacuum to give a dark purple powder. The dark purple solid was then extracted with minimal toluene and the resulting dark purple solution was filtered through Celite. The dark purple solution was then placed in a freezer for recrystallization whereupon dark brown crystals suitable for X-ray diffraction were obtained (1.905 g, 83%). Anal. calcd. for C₆₆H₁₀₄Fe₂N₂O₆: C 69.95, H 9.25, N 2.47; found: C 70.12, H 8.98, N 2.65. MALDI-TOF *m*/*z* (%, ion): 496.479 (100, [M-FeOH]+), 549.399 (10, [M-OH]+), 564.394 (7, [M]+).

Supplementary material

Supplementary spectroscopic and crystal structure data are available with the article through the journal web site at http:// nrcresearchpress.com/doi/suppl/10.1139/cjc-2014-0043. Crystallographic data for CCDC 982453 (H₂L2), CCDC 982454 (1), CCDC 982455 (2), and CCDC 982456 (3) (pdf and cif format) can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/ csd/request/ (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

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