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Iron(III) complexes of pyridine-based tetradentate aminophenol ligands as structural model complexes for the catechol-bound intermediate of catechol dioxygenases

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ABSTRACT

Some pyridine-based tetradentate aminophenol ligands and their acetylacetonato iron(III) LFe(acac) complexes have been synthesized and characterized by spectroscopic techniques, cyclic voltammetry, single crystal X-ray diffraction and magnetic susceptibility studies. X-ray analysis revealed monomer complexes in which the iron centers have been surrounded by pairs of acetyl acetonate and phenolate oxygens and two nitrogen atoms of the ligands. It has been shown that the two Fe– O_{acac} bonds in these complexes are not equal, as seen for Fe– O_{cat} bonds in the catechol-bounded intermediate of catechol dioxygenases. Variable temperature magnetic susceptibility indicates a paramagnetic behavior for all the mononuclear high spin iron complexes. The investigated complexes undergo electrochemical oxidation and reduction.

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1. Introduction

Aromatic hydrocarbons are environmental pollutants which pose a major hazard to the environment, being mutagenic, carcinogenic and recalcitrant [1]. Aromatic ring-cleaving enzymes, such as catechol dioxygenases, play an important role in the degradation of aromatic compounds. This process is common in soil micro-organisms which participate in the recycling of aromatic compounds as sole the carbon and energy sources through aerobic catabolism pathways [2,3]. Catechol dioxygenases catalyze the oxidative cleavage of catechol substrates. These types of enzymes are divided into two subclasses, namely intradiol and extradiol, which differ in their mode of ring cleavage [4–6]. The Fe(III)-containing intradiol dioxygenases cleave the vicinal hydroxyl groups (metacleavage) to yield muconic acid as a product, whereas extradiol dioxygenases catalyze the extradiol ring cleavage at the C-C bond inside the vicinal hydroxyl groups to form α -hydroxymuconic semi-aldehyde [7]. Although intradiol and extradiol dioxygenases oxidize an overlapping set of substrates, they function by two basically different mechanisms due to their different structures [8].

Many attempts to model the catechol dioxygenases have been reported. In this way, iron complexes of tri- and tetradentate ligands containing pyridine, imidazole, pyrazol, carboxylate and phenolate moieties have been synthesized as structural and functional models for these enzymes [9–22]. Among these ligands, tetradentate aminebis(phenolato) ligands have an important role in a designing model for phenol-containing non-heme iron-containing metalloenzymes [23–28]. Many of the reported compounds of amine-bis(phenolato) ligands have focused on the iron acetylacetonato complexes of these ligands [29–32].

In this paper, we present a series of pyridine-based tetradentate aminophenol ligands, $H_2(L^{AMP})$ (Scheme 1) and their acetylacetonato iron(III) complexes, LFe(acac), as enzyme-substrate adduct models for catechol dioxygenases. The phenol moieties and acetylacetone ligand mimic the coordinated tyrosine ligand and Fe–O_{cat} bond in the enzyme-catechol adduct, respectively. The coordination, magnetic and redox properties of related iron complexes of the above mentioned ligands H_2L are described.

2. Materials and methods

Reagents and analytical grade materials were purchased from commercial suppliers and used without further purification, except those for electrochemical measurements. Elemental analyses (C, H, N) were performed by the Isfahan University of Technology. Fourier transform infrared spectroscopy on KBr pellets was performed on a FT IR Bruker Vector 22 instrument. NMR measurements were performed on a Bruker 400 instrument. UV–Vis absorbance digitized spectra were collected using a CARY 100 spectrophotometer. Magnetic susceptibility was measured using powder samples of solid materials in the temperature range 2–300 K by means of a



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Ligand	R ₁	\mathbf{R}_2
H ₂ (L ^{AMPB})	-Br	-Br
$H_2(L^{AMPC})$	-Cl	-Cl
$H_2(L^{AMPBM})$	-C(CH ₃) ₃	-CH ₃
$H_2(L^{AMPOMe})$	-C(CH ₃) ₃	-OCH ₃

Scheme 1. Schematic drawing of tetradentate bisphenolate ligands.

sourd susceptometer (Quantum Design MPMS-XL-5) in a magnetic field of 1000 Oe.

Voltammetric measurements were made with a computer controlled electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PGSTA 30 model and driven by GPES (ECO Chemie). A glassy carbon electrode with a surface area of 0.035 cm² was used as a working electrode and a platinum wire served as the counter electrode. The reference electrode was an Ag wire as the

Table 1

Crystal data and structure refinement for FeL^{AMPB}, FeL^{AMPC}, FeL^{AMPBM} and FeL^{AMPOME}

quasi reference electrode. Ferrocene was added as an internal standard after completion of a set of experiments, and potentials were referenced versus the ferrocenium/ferrocene couple (Fc^+/Fc).

The X-ray data for the reported complexes were collected with an Oxford Sapphire CCD diffractometer using Mo K α radiation, $\lambda = 0.71073$ Å, at 293(2) K, by the ω -2 θ method. The structures were solved by direct methods and refined with the full-matrix least-squares method on F^2 by means of the SHELX97 [33] program package. An analytical absorption correction was applied (RED171 package of programs [34] Oxford Diffraction, 2000), the maximum and minimum transmissions are given in Table 1. The absolute structure for FeL^{AMPOMe} was determined by the Flack method [35], with the Flack x = 0.018(11). Hydrogen atoms were located from the electron density maps and constrained during the refinement.

3. Results

3.1. Preparations

3.1.1. Synthesis of ligands

The syntheses of H_2L^{AMPC} [36], H_2L^{AMPOMe} [37] and H_2L^{AMPBM} [38,39] were conducted by a modified literature procedure, employing the Mannich condensation of the corresponding phenol, amine and formaldehyde without using any more water or methanol, as described below for the synthesis of H_2L^{AMPB} .

3.1.1.1. Synthesis of H_2L^{AMPB} . A mixture of 2,4-di-bromophenol (30.00 mmol), 2-aminomethylpyridine (1.56 mL, 15.00 mmol) and 37% aqueous formaldehyde (2.5 mL, 30.00 mmol) was stirred and refluxed for 48 h. The solvent was decanted, and the remaining yellowish oil was triturated with cold n-hexane and cold methanol

,							
Identification code	FeL ^{AMPB}	FeL ^{AMPC}	FeL ^{AMPBM}	FeL ^{AMPOMe}			
Empirical formula	$C_{25}H_{21}Br_4FeN_2O_4$	$C_{25}H_{21}Cl_4FeN_2O_4$	C ₃₅ H ₄₅ FeN ₂ O ₄	C ₃₅ H ₄₅ FeN ₂ O ₆			
Formula weight	788.93	611.09	613.58	645.58			
T (K)	293(2)	293(2)	293(2)	293(2)			
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073			
Crystal system	trigonal	triclinic	monoclinic	orthorhombic			
Space group	R-3	ΡĪ	$P2_1/n$	P212121			
Unit cell dimensions							
a (Å)	34.7954(13)	12.6710(8)	9.4159(7)	10.4561(3)			
b (Å)	34.7954(13)	13.6811(8)	29.6968(18)	23.3893(6)			
<i>c</i> (Å)	11.8617(4)	17.2776(11)	12.2485(10)	27.7992(8)			
β(°)		109.397(6)	104.977(8)				
V (Å ³)	12437.1(8)	2718.1(3)	3308.6(4)	6798.6(3)			
Ζ	18	4	4	8			
Calculated density (Mg/m ³)	1.896	1.493	1.232	1.261			
Absorption coefficient (mm ⁻¹)	6.362	0.982	0.494	0.489			
F(000)	6894	1244	1308	2744			
Crystal size (mm)	$0.60 \times 0.16 \times 0.12$	$0.38 \times 0.13 \times 0.09$	$0.43 \times 0.38 \times 0.23$	$0.50 \times 0.16 \times 0.12$			
θ (°)	2.19-28.42	2.01-28.37	2.20-28.28	2.13-28.23			
Limiting indices	$-44 \leqslant h \leqslant 46$, $-46 \leqslant k \leqslant 45$,	$-16 \leqslant h \leqslant 15$, $-17 \leqslant k \leqslant 17$,	$-11 \leqslant h \leqslant 10$, $-33 \leqslant k \leqslant 36$,	$-13 \leqslant h \leqslant 13$, $-30 \leqslant k \leqslant 30$,			
	$-14 \leqslant l \leqslant 15$	$-20\leqslant l\leqslant 21$	$-16 \leqslant l \leqslant 16$	$-35 \leqslant l \leqslant 36$			
Reflections collected/unique (R _{int})	27178/6434 (0.0613)	19064/11850 (0.0756)	21125/7331 (0.0826)	46151/14879 (0.0791)			
2θ , completeness (%)	26.00 99.9	25.00 99.0	25.00 99.9	25.00 99.9			
Maximum and minimum transmission	0.5047 and 0.1145	0.9208 and 0.7037	0.8941 and 0.8164	0.9451 and 0.7939			
Data/restraints/parameters	6434/0/325	11850/0/649	7331/0/379	14879/0/793			
Goodness-of-fit (GOF) on F^2	0.955	0.889	1.064	0.813			
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0417, wR_2 = 0.0888$	$R_1 = 0.0616$, $wR_2 = 0.1265$	$R_1 = 0.0792, wR_2 = 0.1843$	$R_1 = 0.0467, wR_2 = 0.0704$			
<i>R</i> indices (all data) Absolute structure parameter	$R_1 = 0.1091, wR_2 = 0.1058$	$R_1 = 0.1667, wR_2 = 0.1700$	$R_1 = 0.1324, wR_2 = 0.2086$	$R_1 = 0.1131, wR_2 = 0.0807$ 0.018(11)			
Largest difference peak and hole (e A ⁻³)	1.408 and -1.073	0.685 and -0.459	0.433 and -0.486	0.378 and -0.302			

to give a creamy yellow powder. The remaining solid residue was washed with cold methanol and boiling water for further purification and then dried in air (4.30 g, 45% yield). ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 3.839 (s, 4H); 3.910 (s, 2H); 7.168 (d, 2H); 7.239 (d, 1H); 7.412 (t, 1H); 7.617 (d, 2H); 7.848 (t, 1H); 8.743 (d, 1H); 11.539 (s, 1H). IR (cm⁻¹): 3446 (OH); 2912 (C–H); 1447 (C=C, phenyl ring). M.p.: 182–183 °C.

3.1.1.2. Synthesis of H_2L^{AMPC} . (4.47 g, 65% yield). ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 3.837 (s, 4H); 3.907 (s, 2H); 6.995 (d, 2H); 7.225 (d, 1H); 7.321 (d, 2H); 7.395 (m, 1H); 7.820 (m, 1H); 8.731 (d, 1H); 11.433 (s, 2H). IR (cm⁻¹): 3432 (OH); 2845 (C–H); 1465 (C=C, phenyl ring). M.p.: 181.2–181.9 °C.

3.1.1.3. Synthesis of H_2L^{AMPOMe} . (5.76 g, 78% yield). ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 1.380 (s, 18H); 3.782 (s, 6H); 3.815 (s, 4H); 3.831 (s, 2H); 6.540 (d, 2H); 6.861 (d, 2H); 7.165 (d, 1H); 7.336 (s, 1H); 7.765 (t, 1H); 8.729(d, 1H); 10.342(s, 2H). IR (cm⁻¹): 3062.87 (OH); 2952.60 (C–H); 1477.3 (C=C, phenyl ring). M.p.: 179.1–180.6 °C.

3.1.1.4. Synthesis of H_2L^{AMPBM} . (4.97 g, 73% yield). ¹H NMR (400 MHz, CDCl3, 298 K) δ : 1.390 (s, 18H); 2.284 (s, 6H); 3.795 (s, 4H); 3.862 (s, 2H); 6.540 (d, 2H); 6.861 (d, 2H); 7.157 (d, 1H); 7.321 (q, 1H); 7.736 (t of d, 1H); 8.735(d, 1H); 10.546 (s, 2H). M.p.: 188.8–190.1 °C.

3.1.2. Synthesis of the complexes

Triethylamine (0.28 ml, 2.00 mmol) was added to a solution of H_2L (1.00 mmol) in ethanol, except in the case of Fe^{AMPC} where the solvent was acetonitrile. Tris(acetylacetonato)iron(III) (0.35 g, 1.00 mmol) was added to this solution and the mixture was refluxed for 2 h, resulting in an intense dark red solution.

3.1.2.1. Synthesis of FeL^{AMPB} . FeL^{AMPB} was crystallized in a 1:1 dichloromethane/ethanol mixture. (0.54 g, 69% yield). Anal. Calc. for $C_{25}H_{21}Br_4FeO_4N_2$ (788.758 g/mol): C, 54.18; H, 3.629; N, 5.070. Found: C, 52.47; H, 3.44; N, 4.69%. IR (KBr, cm⁻¹): 3446, 2901, 1570, 1523, 1453, 1359, 1314, 1271, 1155, 1102, 1016, 936, 849, 795, 708, 545, 491, 451. UV–Vis in CH_2Cl_2 , λ_{max} , nm (ε , M⁻¹ cm⁻¹): 291 (42733), 476 (11351).

3.1.2.2. Synthesis of FeL^{AMPC}. Fe L^{AMPC} was crystallized in a 1:1 acetone and water mixture. (0.45 g, 73% yield). Anal. Calc. for $C_{25}H_{21}$. Cl₄FeO₄N₂ (611.102 g/mol): C, 40.65; H, 2.667; N, 3.632. Found: C, 44.3; H, 3.07; N, 2.18%. IR (KBr, cm⁻¹): 3446, 2910, 1585, 1521, 1456, 1371, 1305, 1269, 1216, 1172, 1091, 1018, 968, 931, 863, 799, 759, 666, 571, 467. UV–Vis in CH₂Cl₂, λ_{max} , nm (ε , M⁻¹ - cm⁻¹): 289 (49657), 480 (12784).

3.1.2.3. Synthesis of FeL^{AMPOMe} . FeL^{AMPOMe} was crystallized in a 1:1:1 dichloromethane/ethanol/acetonitrile mixture. (0.52 g, 80% yield). *Anal.* Calc. for C₃₅H₄₅FeO₆N₂ (645.263 g/mol): C, 65.29; H, 6.814; N, 4.239. Found: C, 65.12; H, 7.03; N, 4.34%. IR (KBr, cm⁻¹): 3446, 2954, 2905, 2868, 1593, 1520, 1470, 1383, 1293, 1200, 1165, 1090, 1017, 922, 870, 837, 759, 543, 476, 437. UV–Vis in CH₂Cl₂, λ_{max} , nm (ε , M⁻¹ cm⁻¹): 232 (39084), 528 (7309).

3.1.2.4. Synthesis of FeL^{AMPBM}. FeL^{AMPBM} was crystallized in a 1:1 dichloromethane/ethanol mixture. (0.46 g, 75% yield). Anal. Calc. for C₃₅H₄₅FeO₄N₂ (613.588 g/mol): C, 68.15; H, 7.196; N, 4.472. Found: C, 68.51; H, 7.39; N, 4.57%. IR (KBr, cm⁻¹): 3413, 2951, 2908, 2355, 1596, 1519, 1458, 1434, 1383, 1261, 1206, 1149, 1090, 1020, 927, 859, 811, 662, 597, 544. UV–Vis in CH₂Cl₂, λ_{max} , nm (ε , M⁻¹ cm⁻¹): 231 (34836), 510 (6552).

4. Discussion

Some pyridine-based tetradentate aminophenol ligands were prepared by a methanol free Mannich condensation of the corresponding phenol, amine and formaldehyde. H_2L^{AMPC} , H_2L^{AMPOMe} and H_2L^{AMPBM} were compared characteristically with those reported in the literature [36–40]. These ligands were treated with an ethanol or acetonitrile solution of tris(acetylacetonato)iron(III) and triethylamine in a suitable ratio, and the solution was refluxed to give the iron complexes FeL^{AMPX} (X: B, C, OMe, BM) in high yields.

In the IR spectra of all the ligands, the OH stretch is observed in the range $3300-3500 \text{ cm}^{-1}$. These strong and sharp bands were replaced by a broad band in the IR spectra of the complexes, proving the coordination of the phenol groups to the metal ion. A strong band was observed in the range $1600-1500 \text{ cm}^{-1}$ related to the carbonyl stretching. The frequency of the CO stretching vibration changes with the variation of the substituents on the phenol groups of the ligands. The electron-donating or accepting properties of the substituents, transmitted through the phenolate and iron atoms, changes the positive charge on the carbonyl carbon, varying the force constant and hence the frequency of the CO stretching vibration.

The electronic spectra of all the complexes were recorded in CH₂Cl₂. The electronic absorption spectra of all the reported complexes show multiple intense bands in the UV and visible regions. In all the complexes, the absorption maxima observed in the near-UV regions (below 300 nm) are caused by $\pi \rightarrow \pi^*$ transitions involving the phenolate units. The lowest energy bands (between 400 and 700 nm) are proposed to arise from charge-transfer transitions from phenolate(π) to Fe(III)(d π^*). The energies of the low-energy LMCT band follow the trend FeL^{AMPB} > FeL^{AMPC} > FeL^{AMPC}. This criteria can be attributed to the transmission of the electron-accepting properties of the halo groups through the phenolate to the iron atoms, which reduces the Fe(III)(d π^*) to Fe(III)(d π^*) transition (Fig. 1).

4.1. Crystal structure determinations of the FeL^{AMPB} , FeL^{AMPC} , FeL^{AMPBM} and FeL^{AMPOMe} complexes

The X-ray experimental data and structure refinement for the crystal structures are summarized in Table 1. Selected bond lengths and angles within the coordination sphere are presented in Table 2.



Fig. 1. Electronic absorption spectra of the synthesized complexes (4.68×10^{-5}) in CH_2Cl_2 solution.

01-Fe1-04

01-Fe1-N2

03-Fe1-N2

01-Fe1-N1

03-Fe1-N1

N2-Fe1-N1

99.27(14)

162.93(14)

80.48(14)

89 26(13)

85.38(12)

76.63(14)

01-Fe1-06

01-Fe1-N2

05-Fe1-N2

01-Fe1-N1

05-Fe1-N1

N2-Fe1-N1

Table 2

01-Fe1-04

01-Fe1-N2

03-Fe1-N2

01-Fe1-N1

03-Fe1-N1

N2-Fe1-N1

96.66(13)

94.61(13)

85 25(12)

77.92(13)

173.60(13)

100.24(12)

01-Fe1-04

01-Fe1-N2

03-Fe1-N2

01-Fe1-N1

03-Fe1-N1

N2-Fe1-N1

90.62(16)

85.29(16)

84.02(16)

92.01(15)

88.37(15)

76.76(15)

Selected bond lengths (Å) and angles (°) for the coordination sphere of the central Fe ion for FeL ^{AMPB} , FeL ^{AMPE} , FeL ^{AMPBM} and FeL ^{AMPOMe} .										
FeL ^{AMPB}	FeL ^{AMPB}	FeL ^{AMPC}	Mol. 1	FeL ^{AMPC}	Mol. 2	FeL ^{AMPBM}	FeL ^{AMPBM}	FeL ^{AMPOMe}	Mol. 1	FeL ^{AMPOMe}
Fe1-01	1.920(3)	Fe1-01	1.925(4)	Fe2-05	1.911(4)	Fe1-01	1.890(3)	Fe1-01	1.925(2)	Fe2-021
Fe1-02	1.943(3)	Fe1-02	1.926(3)	Fe2-06	1.922(4)	Fe1-02	1.894(3)	Fe1-02	1.873(2)	Fe2-022
Fe1-04	1.963(3)	Fe1-04	1.976(4)	Fe2-07	1.970(4)	Fe1-03	2.071(3)	Fe1-05	2.089(2)	Fe2-025
Fe1-03	1.987(3)	Fe1-03	2.044(4)	Fe2-08	2.044(4)	Fe1-04	1.975(3)	Fe1-06	1.974(2)	Fe2-026
Fe1-N2	2.174(3)	Fe1-N2	2.187(4)	Fe2-N4	2.199(4)	Fe1-N2	2.199(4)	Fe1-N2	2.194(3)	Fe2-N22
Fe1-N1	2.234(3)	Fe1-N1	2.187(4)	Fe2–N3	2.188(4)	Fe1-N1	2.201(4)	Fe1-N1	2.215(3)	Fe2-N21
01-Fe1-02	172 96(13)	01-Fe1-02	99.97(15)	05-Fe2-06	99 39(16)	01-Fe1-02	101 57(13)	02-Fe1-01	10151(9)	021_Fe2_022

90.91(15)

92.23(15)

88.49(16)

85 38(16)

84.45(16)

77.01(16)

05-Fe2-07

05-Fe2-N3

08-Fe2-N3

05-Fe2-N4

08-Fe2-N4

N3-Fe2-N4



Fig. 2. ORTEP diagram and atom labeling scheme for the complex FeL^{AMPB}. The atomic ellipsoids are plotted at the 30% probability level.

Complexes similar to these reported here were designed as small-molecular models of enzymes, in particular catechol 1,2dioxygenases [24,31,38]. In that enzyme, the research revealed a multi-step binding of the substrate and inhibitors, with the conversion of the Fe coordination sphere from trigonal bypyramidal into octahedral [41,42]. The trigonal bypyramidal geometry is known for Fe(III) complexes with diamine-bis(phenolate) ligands and monodentate Cl or Br counterions [38]. On the contrary, the use

of the acac bidentate ligand resulted in an octahedral geometry of the coordination sphere of Fe(III) or Mn(III) complexes [31]. In all the complexes reported here, the coordination sphere is octahedral (Table 2, Figs. 2-5). In the catechol 1,2-dioxygenases, the coordination sphere of Fe is formed by two tyrosine residues (Y408 and Y477) occupying a cis orientation, two histidine residues and a water or OH group. It was suggested, that the equatorial Y408 is a Lewis base affecting the Lewis acidity of the central Fe ion and facilitating the rapid exchange of ligands in the catalytic cycle [41]. Tyrosine occupies the trans position relative to one of the catechol oxygens. One of the histidine residues is positioned trans relative to the other catechol oxygen.

96.18(9)

89.43(9)

88 21(9)

86.05(9)

76.36(10)

80.80(10)

021-Fe2-026

021-Fe2-N22

025-Fe2-N22

021-Fe2-N21

025-Fe2-N21

N22-Fe2-N21

Mol. 2 1.882(2) 1.937(2) 1.962(2)2.092(2)2.201(3)2.203(2)101 19(9)

87.86(10)

163.01(10)

91.94(10) 90 51(9)

167.02(10)

76.69(10)

In the FeL^{AMPC}. FeL^{AMPBM} and FeL^{AMPOMe} complexes reported here, the coordination sphere is octahedral with the tetradentate amino-pyridyl-bis(phenolate) and bidentate acac ligands. The relative position of the two phenolate moieties in the coordination sphere is cis (Figs. 3-5). One phenolate O and the ternary N1 are positioned trans relative to the acac oxygen atoms. Such an architecture resembles that suggested for catechol 1,2-dioxygenases. On the contrary, in FeL^{AMPB}, the acac oxygen atoms are positioned trans to the tertiary N1 and pyridil N2 atoms, while the phenolate O atoms are trans to each other (Fig. 2). In all the structures reported in this paper, the bond distances for the analogous bonds within the Fe coordination sphere are similar to each other, with the Fe–O bonds formed by the phenolate oxygens being the shortest, while the Fe–N bonds are the longest within the sphere (Ta-ble 2). It has to be noted that in FeL^{AMPC} and FeL^{AMPBM} there is no statistically significant difference in the length of the Fe-O coordination bonds formed by both phenolates. However, in the FeL^{AMPB}



Fig. 3. ORTEP diagram and atom labeling scheme for two molecules of the complex FeL^{AMPC}, constituting the asymmetric part of the structure. The atomic ellipsoids are plotted at the 30% probability level. The hydrogen atoms are omitted for clarity.



Fig. 4. ORTEP diagram and atom labeling scheme for the complex FeL^{AMPBM}. The atomic ellipsoids are plotted at the 30% probability level. The hydrogen atoms are omitted for clarity.

and FeL^{AMPOMe} complexes, the difference between these bonds is significant (0.02 and 0.05 Å, respectively). This seems to be consistent with the different role of both tyrosine residues mentioned above, as concluded for catechol 1,2-dioxygenase [41]. Also, it has to be noted, that the Fe–O(phenolate) distances for the chlorinated or brominated ligands are significantly longer than those found for the FeL^{AMPDM} and FeL^{AMPOMe} complexes (Table 2). The two different distances found for FeL^{AMPOMe} can be classified as belonging to one of the groups mentioned above. These bond lengths are similar to the Fe–O(phenolato) bond lengths observed in related octahedral iron(III) complexes possessing phenolato ligands [29–32]. They are, however, longer than the average Fe–O bond length in trigonal bipyramidal or square pyramidal complexes, as expected because of the higher coordination number [12,38].

In FeL^{AMPC}, the distance between the iron atom and the central nitrogen of the ligand is shorter than the previously reported Fe–N distance of (amine)bis(phenolato)Fe(acac) complexes. However, in the other three structures this bond length is longer than the related Fe–N distance of the related octahedral complexes [29–32]. In FeL^{AMPBM}, the Fe1–N1 distance is shorter than the corresponding

Table 3

Electrode potentials (in V) for the oxidation and reduction of the complexes FeL^{AMPB}, FeL^{AMPC}, FeL^{AMPOMe} and FeL^{AMPBM} measured at T = -70 °C in CH₂Cl₂ solutions and referenced vs. the Fc⁺/Fc couple. The scan rate is 25 mV/s.

Complexes	$E_1^{\rm red}$ (V)	$E_2^{\rm red}$ (V)	$E_1^{\text{ox}}(V)$	$E_2^{\mathrm{ox}}(V)$
FeL ^{AMPB}	-0.74^{a}	-1.25 ^a	0.74 ^a	1.11 ^a
FeL ^{AMPOMe}	- -1.36ª	-0.96 ^a -1.67 ^b	0.91 ^b 0.12 ^b	1.20 ^a 0.47 ^b
FeL ^{AMPBM}	-1.49^{a}	-1.75^{a}	0.16 ^b	0.65 ^b

^a Irreversible reaction, peak potential is given.

^b Electrochemical quasi-reversible reaction.

Fe–N distance of 2.2706(15) Å in the trigonal bipyramidal complex employing the same ligand, in which the central nitrogen atom of the ligand and the chloride ion occupy the apical sites [38].

X-ray crystal structure analysis revealed that the dihedral angle between the two phenolate rings are 61.2° and 58.3°, 72.8° and 73.3° and 71.1° for the FeL^{AMPC}, FeL^{AMPBM} and FeL^{AMPOMe} complexes respectively. In the FeL^{AMPB} complex, with a flat arrangement of the phenolic rings of the ligand, the angle is 45.3°.

The packing analysis of the reported structures revealed some intermolecular interactions that are listed in Table 3.

4.1.1. Crystal structure of FeL^{AMPB}

The structure of FeL^{AMPB} consists of a single molecule of the complex (Fig. 2). The bond distances and bond angles relevant to the octahedral coordination sphere of the complex are listed in Table 2. The coordination arrangement around the iron atom of this complex is different from the trigonal bypyramidal arrangement found for the active site of the PCA-bound intermediate of 3,4-PCD [3]. Both acac oxygen atoms of the complex have a trans position relative to the nitrogen atoms of the ligand, but the catechol oxygen atoms in 3,4-PCD are trans to the nitrogen atom of His460 and the oxygen atom of Tyr408. The Fe–O_{acac} bond lengths (1.963(3) and 1.987(3) Å) of this complex are longer than the Fe-Ocat bond lengths in 3,4-PCD [3], the distance of Fe-O3 trans to the pyridine group is longer than that of Fe-O4 trans to the tertiary amine ligand. This indicates that the pyridine ligand has a greater trans influence than the tertiary amine ligand in the FeL^{AMPB} complex. The Fe-O1 and Fe-O2 (phenolato) bond lengths (1.920(3) and 1.943(3) Å, respectively) agree with the Fe–O (Y408) bond length (2.199(4) Å) of the PCA-bound intermediate of 3,4-PCD [3] (Table 2).

The extended conformation unique for that complex is reflected in the torsion angles C6–C7–N1–C8 and C7–N1–C8–C9 of 176.1(4)° and 179.3(4)°. Other torsion angles describing the molecular



Fig. 5. ORTEP diagram and atom labeling scheme for the asymmetric part of the complex FeL^{AMPOMe}. The atomic ellipsoids are plotted at the 30% probability level. The hydrogen atoms are omitted for clarity.

conformation are N1–C15–C16–N2 of $-32.9(5)^{\circ}$, and the bridge C1–C6–C7–N1 and N1–C8–C9–C1 angles of $-46.3(6)^{\circ}$ –and $60.4(5)^{\circ}$, respectively.

The L^{AMPB} ligand is bound with two phenolate O atoms in trans positions. For the observed flat arrangement of the ligand, the dihedral angle between the best planes of the two phenolate rings is 45.3°. The acac ligand is positioned almost perpendicular to the L^{AMPB} ligand, with the dihedral angle between its plane and the phenolate ring planes being 67.0(1)° and 67.8(1)° for the C1–C6 and C9–C14 rings, respectively. The dihedral angles between the best planes of the pyridine ring and C1–C6, C9–C14 and acac are 77.6(2)°, 33.4(2)° and 37.4(1)°, respectively.

Five-membered and six-membered chelate rings are formed by the ligands. Among those, Fe–N1–C15–C16–N2 has a conformation twisted on N1–C15, Fe1–O1–C1–C6–C7–N1 is half-chair, Fe1–O2–C14–C9–C8–N1 has a boat conformation and Fe1–O3–C22–C23–C24–O4 is an envelope.

4.1.2. Crystal structure of FeL^{AMPC}

The asymmetric part of the structure consists of two molecules of FeL^{AMPC} with the geometry corresponding to the octahedral mode for catechol 1,2-dioxygenase. Two phenolate rings are positioned trans (Fig. 3) and the different dihedral angles between their best planes are 61.2° and 58.3° for Molecules 1 and 2, respectively. These values are smaller by 10° than those found in FeL^{AMPBM} and FeL^{AMPOMe} reported later in this paper.

The molecular conformation is slightly different from that detected for FeL^{AMPB}, which is reflected by the N1–C15–C16–N2 torsion angle of $-16.7(7)^{\circ}$, and the C1–C6–C7–N1, C6–C7–N1–C8, C7–N1–C8–C9 and N1–C8–C9–C14 bridge torsion angles of 56.6(6)°, $-179.7(4)^{\circ}$, 53.3(5)° and 46.1(7)°, respectively. A similar conformation is found for Molecule 2, with the corresponding values being $-16.6(7)^{\circ}$, 57.7(6)°, 177.8(4)°, 56.6(6)° and 38.9(7)°. The dihedral angles between the acac plane and the phenolate C1–C6 and C9–C14 rings are 37.6(2)° and 82.7(2)° for Molecule 1 and 37.2(2) and 86.8(2)° for Molecule 2. The dihedral angles between the best planes of the pyridine ring and C1–C6, C9–C14 and acac or their equivalents are 55.5(2)°, 10.6(4)° and 87.2(2)° and 57.2(2)°, 15.5(3)° and 85.7(2)° for Molecules 1 and 2, respectively.

Among the chelate rings formed by the ligands in Molecule 1, Fe–N1–C15–C16–N2 is an envelope on N1, Fe1–O1–C1–C6–C7–N1 is a screw-boat, Fe1–O2–C14–C9–C8–N1 has an envelope conformation, while Fe1–O3–C22–C23–C24–O4 is planar. In Molecule 2, the ring Fe2–N3–C45–C46–N4 is an envelope on N3, Fe2–O5–C31–C36–C37–N3 is a screw-boat, Fe2–O6–C44–C39–C38–N3 is an envelope and Fe1–O7–C52–C53–C54–O8 is planar.

4.1.3. Crystal structure of FeL^{AMPBM}

The asymmetric part of the structure consists of a molecule of FeL^{AMPBM} with an octahedral geometry of the coordination sphere (Fig. 4), analogous to FeL^{AMPC}. The two phenolate rings are positioned cis and the dihedral angles between their best planes, being 72.8°, is significantly larger than those found in the two molecules of FeL^{AMPC}, as described above. The molecular conformation is reflected by the N1–C25–C26–N2 torsion angle of 34.8(6)° and the C1–C6–C7–N1, C6–C7–N1–C8, C7–N1–C8–C9 and N1–C8–C9–C14 bridge torsion angles of $-58.2(5)^\circ$, $-55.9(5)^\circ$, $171.7(4)^\circ$ and $-62.3(5)^\circ$, respectively. The dihedral angles between the acac plane and the phenolate C1–C6 and C9–C14 rings are $42.2(2)^\circ$ and $30.6(2)^\circ$. The dihedral angles between the best planes of the pyridine ring and C1–C6, C9–C14 and acac are $30.6(2)^\circ$, $42.2(4)^\circ$ and $82.7(2)^\circ$, respectively.

Among the chelate rings formed by the ligands in Molecule 1, the Fe-N1-C25-C26-N2 is twisted on N1-C25, Fe1-O1-C1-C6-C7-N1 and Fe1-O2-C14-C9-C8-N1 are in a boat conformation, while Fe1-O3-C22-C23-C24-O4 has an envelope conformation.

4.1.4. Crystal structure of FeL^{AMPOMe}

The absolute structure of the complex was determined according to the Flack method [19]. The asymmetric part of the structure consists of two molecules of FeL^{AMPOMe}, with an octahedral geometry of the coordination sphere (Fig. 5). In both molecules the phenolate rings are positioned cis and are almost perpendicular in the coordination sphere, the dihedral angles between their best planes are 73.28(9)° and 71.1(1)° for Molecules 1 and 2, respectively. These values are similar to those found in FeL^{AMPBM} and FeL^{AMPC}.

The conformation of both molecules is similar to that observed for FeL^{AMPBM}. In Molecule 1, the N1–C25–C26–N2 torsion angle is $36.5(4)^{\circ}$ and the C1–C6–C7–N1, C6–C7–N1–C8, C7–N1–C8–C9 and N1–C8–C9–C14 bridge torsion angles are -65.1(5), 170.3(3), -59.5(3) and $-59.2(4)^{\circ}$, respectively. For Molecule 2, the corresponding values are $-36.2(4)^{\circ}$, $60.9(4)^{\circ}$, $58.9(3)^{\circ}$, $-170.5(3)^{\circ}$ and $65.2(4)^{\circ}$.

The dihedral angles between the acac plane and the phenolate C1–C6 and C9–C14 rings are 59.37(7)° and 68.61(7)° for Molecule 1 and 68.19(9)° and 45.7(1)° for Molecule 2. The dihedral angles between the best planes of the pyridine ring and C1–C6, C9–C14 and acac or their equivalents are 40.7(1), 32.6(1)° and 57.61(6)° and 33.0(1)°, 38.1(1)° and 81.1(1)° for Molecules 1 and 2, respectively.

For the chelate rings formed by the ligands in Molecule 1, the Fe–N1–C25–C26–N2 is twisted on N1–C25, Fe1–O1–C1–C6–C7–N1 and Fe1–O2–C14–C9–C8–N1 have a boat conformation, while Fe1–O3–C22–C23–C24–O4 is planar. In Molecule 2, the ring Fe2–N21–C65–C66–N22 is twisted on N21–C65, Fe2–O21–C41–C46–C47–N21 and Fe2–O22–C54–C49–C48–N21 are in a boat conformation and Fe2–O25–C72–C73–C74–O26 is a screw-boat.

4.2. Magnetic susceptibility measurements

Magnetic susceptibilities for powdered samples of FeL^{AMPB}, FeL^{AMPC}, FeL^{AMPOMe} and FeL^{AMPBM} were measured in a magnetic field of 1000 Oe as a function of temperature in the range 2–300 K. The measured data were corrected for the temperature-independent Larmor diamagnetic susceptibility obtained from Pascal's tables [43] and for the sample holder contribution. The temperature variation of the susceptibility $\chi(T)$ and the effective magnetic moment μ_{eff} in Bohr magnetons (BM) are shown in Fig. 6. The susceptibilities of all four samples are practically the same and follow a Curie 1/*T* law, indicating paramagnetic behavior,



Fig. 6. Temperature dependent susceptibility $\chi(T)$ and effective magnetic moment μ_{eff} (inset) of FeL^{AMPX} (X = B, C, OMe, BM) measured in a magnetic field of *H* = 1000 Oe.

which has also been reported for LFe(acac) down to 20 K in [29]. Paramagnetic behavior can also be observed from the temperature independent effective magnetic moment of the complexes. The effective magnetic moments for all the complexes lie between 5.7 and 5.8 BM, which agrees with the expected effective magnetic moment of a high spin Fe³⁺ ion of 5.9 BM [44]. Similar values of the effective magnetic moment at room temperatures have been reported for high-spin octahedral Fe^{III} complexes in [30]. A small downturn of the measured effective moment at very low temperatures can be attributed to a zero field splitting [45] rather than a weak antiferromagnetic interaction.

4.3. Electrochemistry

The cyclic voltammograms (CVs) of all the complexes have been recorded in CH_2Cl_2 solutions containing 0.1 M $[(nBu)_4N]ClO_4$ as a supporting electrolyte. Prior to the measurements, the GC electrode was polished with 0.1 mm alumina powder and washed with distilled water. The voltage scan rate was set at 25 mV sec⁻¹. The solutions were deoxygenated by bubbling nitrogen gas through them. The cyclic voltammograms (CVs) show electrochemical oxidation and reduction peaks for the iron complexes (Fig.7 and Table 3).

The oxidation processes were assigned to a ligand-centered oxidation, yielding the phenoxyl radical in the complex. This ligand-centered voltammogram is electrochemically irreversible for the E_2^{OX} FeL^{AMPB} complex, as is seen from the separation of the oxidation and reduction peaks ($\Delta Ep = Epa - Epc$). In addition, the current relationship (ipa/ipc) is less than unity in each case. For the FeL^{AMPC}, FeL^{AMPOMe} and FeL^{AMPBM} complexes, ligand-centered voltammograms are electrochemically quasi-reversible, based on the deviation of ΔEp from 1. The electrochemical behavior of the FeL^{AMPOMe} and FeL^{AMPBM} complexes is consistent with electrochemical studies on related Fe(acac) complexes bearing an (amine)-bis(phenolato) ligand with an N,N-dimethyl-1,2- or 2methoxyethylamin arm [32]. However the FeL^{AMPBM} complex, despite it being a similar complex with a 2-methoxyethylamin arm, exhibits irreversible oxidation responses [30]. This may be attributed to the more electron accepting pyridyl arm than the 2-methoxyethylamin arm, which is likely to destabilize the phenoxyl radical. Metal-centered voltammograms have been observed in the negative potential range, which correspond to the Fe(III)/Fe(II) reduction of the complexes. The Fe(III)/Fe(II) redox potentials are



Fig. 7. Cyclic voltammogramms of the FeL^{AMPOMe} and FeL^{AMPBM} complexes in CH_2Cl_2 with $[(nBu)_4N]ClO_4$ as the supporting electrolyte. Potentials are referenced vs. Fc, the scan rate is 25 mV/s and T = -70 °C.

observed to shift to more negative values on varying the substituents on the phenolato group from electron withdrawing $(R_1 = R_2 = -Cl, -Br)$ to electron donating $(R_1 = -C(CH_3)_3, R_2 = -CH_3)$ due to the lower Lewis acidity of the iron centers.

5. Conclusions

A few iron(III) complexes of the type FeL^{AMPX}, where L is a synthesized [N-O]-donor tripodal ligand containing a 2-aminomethylpyridine derivative of aminophenol, have been isolated and studied as structural models for substrate adducts of catechol dioxygenases. The X-ray crystal structures of the complexes reveal that these complexes have monomer crystal structures, in which iron centers have been surrounded by two acetylacetonate and phenolate oxygens and two nitrogens of the ligands. The two Fe–O_{acac} bonds in the complexes are different in length, as is seen for the iron-catechol oxygen bonds (Fe–O_{cat}) in the catechol-bounded intermediate of catechol dioxygenases.

Magnetostructural studies of all the complexes displayed a paramagnetic high spin iron(III) complex in almost the whole investigated temperature range. Oxidation and reduction of the investigated complexes yielded the corresponding oxidized or reduced species due to ligand or metal centered electrochemical process.

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Appendix A. Supplementary data

The structural data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 882058, 882059, 882060 and 882061 for FeL^{AMPB}, FeL^{AMPC}, FeL^{AMPBM} and FeL^{AMPOMe}, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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