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## Structural flexibility within a sterically hindered ligand platform: mononuclear iron(II) carboxylate complexes as subsite models for diiron(II) centers

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Dedicated to Professor Kenneth N. Raymond on the occasion of his 60th birthday

#### Abstract

The synthesis and characterization of a series of mononuclear iron(II) carboxylate complexes are described. By using sterically hindered carboxylate ligands, 2,6-di(*p*-tolyl)benzoate ( $Ar^{Tol}CO_2^{-}$ ) and 2,6-di(*4-tert*-butylphenyl)benzoate ( $Ar^{4-tBuPh}CO_2^{-}$ ), a series of four-, five-, and six-coordinate iron(II) complexes were synthesized. The compounds are [Fe(O<sub>2</sub>CAr<sup>Tol</sup>)<sub>2</sub>(1-BnIm)<sub>2</sub>] (**3**), [Fe(O<sub>2</sub>CAr<sup>Tol</sup>)<sub>2</sub>(1-MeBzIm)<sub>2</sub>] (**4**), [Fe(O<sub>2</sub>CAr<sup>4-tBuPh</sup>)<sub>2</sub>(2,2'-bipy)<sub>2</sub>] (**5**), [Fe(O<sub>2</sub>CAr<sup>Tol</sup>)<sub>2</sub>(TMEDA)] (**6**), and [Fe(O<sub>2</sub>CAr<sup>Tol</sup>)<sub>2</sub>(BPTA)] (**7**). Structural analyses of **3**–7 revealed that the overall stereochemistry of the [Fe(O<sub>2</sub>CAr')<sub>2</sub>L<sub>n</sub>] units is dictated by electronic and steric factors of the N-donor ligands (L), as well as by the flexible coordination of the carboxylate ligands. Distinctive Mössbauer parameters obtained for these and related compounds facilitated the spectral assignment of a diiron(II) complex having asymmetric metal sites, [Fe<sub>2</sub>( $\mu$ -O<sub>2</sub>CAr<sup>Tol</sup>)<sub>3</sub>(O<sub>2</sub>CAr<sup>Tol</sup>)(2,6-lutidine)] (**2**). Well-defined mononuclear iron carboxylate complexes thus may serve as subsite models for higher nuclearity species in both synthetic and biological systems.

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Keywords: Carboxylate shifts; Mononuclear iron complexes; Mössbauer spectroscopy; m-Terphenyl

#### 1. Introduction

Coordinatively unsaturated redox-active transition metal ions bind and activate small molecule substrates in living systems [1]. Sulfido-bridged three-coordinate iron centers occur in the nitrogen-fixing FeMo cofactors [2]. One carboxylate and two histidine ligands bind nonheme iron in selected dioxygen-activating enzymes [3– 5]. Efforts to investigate structure–function relationships for such catalytic sites have been greatly assisted by low molecular weight analogs having similar chemical properties [6,7].

Sterically hindered ligands are commonly exploited to stabilize low-coordinate metal centers [8,9]. Among the tactics used to afford steric bulk is the *m*-terphenyl

fragment, which can support unusual coordination geometries in mononuclear complexes. The two-coordinate iron(II) thiolate complexes [Fe(SAr<sup>Mes</sup>)- $\{N(SiMe_3)_2\}$ ] and [Fe(SAr<sup>Mes</sup>)\_2] [10,11] illustrate this application. Two mesityl groups flanking the metal binding sites apparently shield them against unwanted oligomerization reactions. Control over coordination number and geometry can thus be achieved by interligand steric interactions in the second coordination sphere.

Recently, we [12–15] and others [16,17] have employed the *m*-terphenyl fragment to access coordinatively unsaturated diiron carboxylate complexes. Following a divergent synthetic route, a variety of tetracarboxylate diiron(II) compounds were prepared from a convenient synthetic precursor,  $[Fe_2(\mu-O_2-CAr^{Tol})_2(O_2CAr^{Tol})_2(THF)_2]$  (1), where  $Ar^{Tol}CO_2^- = 2,6$ -di(*p*-tolyl)benzoate [12]. Weakly coordinating THF molecules in 1 are readily displaced by N-donor ligands under mild conditions to afford diiron(II) complexes

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bearing a close structural resemblance to the active sites of selected non-heme diiron enzymes [3,18,19]. These ligand substitution reactions, together with the flexible coordination of the terphenyl carboxylates, afforded doubly-, triply-, and quadruply-bridged diiron complexes sharing the common  $\{Fe_2(O_2CAr^{Tol})_4\}$  component [12,13,20]. In an extension of this approach we explored the chemistry of sterically more demanding monodentate and polydentate N-donor ligands. Our goal was to evaluate how variation in steric bulk and ligand donor strength would affect the nuclearity and coordination geometry of the resulting complexes.

In this report, we describe the synthesis and characterization of neutral mononuclear iron(II) complexes of the carboxylate ligands  $Ar'CO_2^-$  ( $Ar' = Ar^{Tol}$  or Ar<sup>4-tBuPh</sup>). Four-, five-, and six-coordinate compounds were readily obtained from a common synthetic precursor with the proper choice of N-donor ligands. Unique structural and physical properties of the compounds [Fe(O<sub>2</sub>CAr')<sub>2</sub>L<sub>n</sub>] (L = 1-BnIm (3); 1-MeBzIm (4); 2,2'-bipy (5); TMEDA (6); BPTA (7)) are described. The Mössbauer parameters of these compounds were used to facilitate spectral assignment of [Fe2(µ-O2C- $Ar^{Tol}_{3}(O_2CAr^{Tol})(2,6-lutidine)$ ] (2), which has asymmetric iron centers. Carboxylate shifts upon changes in the N-donor ligands and their structural implications are discussed. A portion of this work has been previously communicated [15].

#### 2. Experimental

#### 2.1. Materials and methods

All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Dichloromethane was distilled over CaH<sub>2</sub> under nitrogen. Diethyl ether, pentanes, and THF were saturated with nitrogen and purified by passage through activated Al<sub>2</sub>O<sub>3</sub> columns under nitrogen [21]. The compounds Fe(OTf)<sub>2</sub>·2MeCN [22], 2,6-di(*p*-tolyl)benzoic acid (Ar<sup>Tol</sup>CO<sub>2</sub>H) [23–25], *N*,*N*'-bis(2-pyridylmethyl)-*tert*butylamine (BPTA) [26], and [Fe<sub>2</sub>( $\mu$ -O<sub>2</sub>CAr<sup>Tol</sup>)<sub>2</sub>(O<sub>2</sub>-  $CAr^{Tol}_{2}(THF)_{2}$  (1) [12] were prepared according to literature procedures. The syntheses of 2,6-di(4-*tert*butylphenyl)benzoic acid (Ar<sup>4-tBuPh</sup>CO<sub>2</sub>H) and [Fe<sub>2</sub>( $\mu$ -O<sub>2</sub>CAr<sup>Tol</sup>)<sub>3</sub>(O<sub>2</sub>CAr<sup>Tol</sup>)(2,6-lutidine)] (2) are reported elsewhere [20]. Air-sensitive manipulations were carried out under nitrogen in a Vacuum Atmospheres drybox or by standard Schlenk line techniques.

#### 2.2. Physical measurements

FT-IR spectra were recorded on a Bio Rad FTS-135 instrument with Win-IR software. UV–Vis spectra were measured on a Hewlett-Packard 8453 diode array spectrophotometer. Mössbauer spectra were obtained on an MS1 spectrometer (WEB Research Co.) with a <sup>57</sup>Co source in a Rh matrix maintained at room temperature (r.t.) in the MIT Department of Chemistry Instrumentation Facility. Solid samples were prepared by suspending ~ 0.05 mmol of the powdered material in Apeizon N grease and packing the mixture into a nylon sample holder. All data were collected at 4.2 K and the isomer shift ( $\delta$ ) values are reported with respect to natural iron foil that was used for velocity calibration at r.t. The spectra were fit to Lorentzian lines by using the WMOSS plot and fit program [27].

#### 2.3. Preparation of compounds

2.3.1.  $[Fe(O_2CAr^{Tol})_2(1-BnIm)_2]$  (3)

To a rapidly stirred pale yellow CH<sub>2</sub>Cl<sub>2</sub> (2 ml) solution of 1 (98 mg, 67 µmol) was added dropwise 1benzylimidazole (1-BnIm) (43 mg, 0.27 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 ml). The resulting colorless solution was stirred for 3 h and filtered. Vapor diffusion of pentanes into the filtrate afforded colorless blocks of 3 (102 mg, 0.105 mmol, 78%), which were suitable for X-ray crystallography. FT-IR (KBr,  $cm^{-1}$ ) 3141(w), 3121(m), 2920(w), 1608(vs), 1585(vs), 1515(vs), 1497(m), 1454(vs), 1438(m), 1400(m), 1346(vs), 1305(m), 1283(m), 1239(m), 1144(w), 1106(s), 1088(s), 1031(m), 1020(m), 946(m), 940(w), 838(s), 820(s), 800(s), 783(s), 765(s), 752(s), 736(s), 725(s), 708(s), 693(s), 655(s), 544(m), 458(w). Anal. Calc. for C<sub>62</sub>H<sub>54</sub>FeN<sub>4</sub>O<sub>4</sub>:

3

C, 76.38; H, 5.58; N, 5.75. Found: C, 75.83; H, 5.92; N, 5.75%.

## 2.3.2. $[Fe(O_2CAr^{Tol})_2(1-MeBzIm)_2]$ (4)

To a rapidly stirred pale yellow CH<sub>2</sub>Cl<sub>2</sub> (3 ml) solution of 1 (101 mg, 69.1 µmol) was added dropwise 1-methylbenzimidazole (1-MeBzIm) (39 mg, 0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml). The reaction immediately turned into a heterogeneous mixture. Volatile fractions were removed under reduced pressure and the residual offwhite solid was extracted into MeOH-MeCN (1:1, 3 ml) and filtered. Vapor diffusion of Et<sub>2</sub>O into the filtrate afforded colorless blocks of 4 (103 mg, 0.112 mmol, 81%), which were suitable for X-ray crystallography. FT-IR (KBr,  $cm^{-1}$ ) 3111(w), 3056(m), 2918(m), 1513(vs), 1565(vs), 1453(vs), 1361(vs), 1297(m), 1255(m), 12039(s), 1186(m), 1149(m), 1130(w). 1111(w), 1071(w), 1020(w), 1006(w), 916(w), 882(m), 855(m), 835(m), 821(m), 802(m), 784(m), 763(s), 586(w), 541(w), 525(w), 454(vw). Anal. Calc. for C<sub>58</sub>H<sub>50</sub>FeN<sub>4</sub>O<sub>4</sub>: C, 75.48; H, 5.46; N, 6.07. Found: C, 75.50; H, 5.42; N, 6.12%.

## 2.3.3. $[Fe(O_2CAr^{4-tBuPh})_2(2,2'-bipy)]$ (5)

To a rapidly stirred MeCN (5 ml) solution of Fe(OTf)<sub>2</sub>·2MeCN (112 mg, 0.257 mmol) was added NaO<sub>2</sub>CAr<sup>4-tBuPh</sup> (208 mg, 0.509 mmol) to afford a pale vellow solution. A portion of 2,2'-bipyridine (2,2'-bipy) (40 mg, 0.256 mmol) in MeCN (3 ml) was added dropwise. The color of the solution turned dark burgundy red and crystalline material began to deposit within minutes. Dark red blocks of 5 (150 mg, 56%) were isolated and analyzed by X-ray crystallography. FT-IR (KBr,  $cm^{-1}$ ) 3057(m), 2962(s), 2903(s), 2866(s), 1598(vs), 1579(vs), 1547(vs), 1513(vs), 1473(s), 1460(vs), 1442(vs), 1406(s), 1381(vs), 1363(vs), 1268(m), 1020(m), 856(m), 842(m), 827(m), 806(m), 781(s), 763(s), 752(m), 736(m), 695(w), 686(w), 578(s); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>) ( $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)) 350 (sh, 290), 537 (200). Anal. Calc. for C<sub>64</sub>H<sub>66</sub>FeN<sub>2</sub>O<sub>4</sub>: C, 78.19; H, 6.77; N, 2.85. Found: C, 78.10; H, 6.83; N, 2.84%.

## 2.3.4. $[Fe(O_2CAr^{Tol})_2(TMEDA)]$ (6)

2.3.4.1. Method A. A portion of N,N,N',N'-tetramethylethylenediamine (TMEDA) (75 µl, 0.497 mmol) was added dropwise to a rapidly stirred MeCN (10 ml) solution of Fe(OTf)<sub>2</sub>·2MeCN (219 mg, 0.502 mmol). The colorless solution was treated with NaO<sub>2</sub>CAr<sup>Tol</sup> (325 mg, 1.00 mmol) and the heterogeneous mixture was stirred overnight. Volatile fractions were removed under reduced pressure and the residual off-white solid was extracted into CH<sub>2</sub>Cl<sub>2</sub> (5 ml). Insoluble material was filtered off and pentanes–hexanes (1:1) were allowed to diffuse into the pale yellow filtrate at r.t. Colorless blocks of **6** (308 mg, 80%) were obtained and analyzed by X-ray crystallography.

2.3.4.2. Method B. To a rapidly stirred  $CH_2Cl_2$  (3 ml) solution of **1** (153 mg, 0.105 mmol) was added dropwise TMEDA (32 µl, 0.21 mmol). The reaction mixture was stirred for 0.5 h and filtered. Vapor diffusion of pentanes-hexanes (1:1) into the filtrate afforded colorless blocks of **6** (148 mg, 91%). FT-IR (KBr, cm<sup>-1</sup>) 2916(m), 2865(m), 1545(vs), 1514(vs), 1459(vs), 1411(s), 1382(vs), 1291(w), 1125(w), 1112(w), 1029(m), 954(w), 855(m), 835(m), 818(m), 800(vs), 766(s), 738(m), 711(s), 586(m), 546(m), 528(s). Anal. Calc. for C<sub>48</sub>H<sub>50</sub>FeN<sub>2</sub>O<sub>4</sub>: C, 74.41; H, 6.50; N, 3.62. Found: C, 74.56; H, 6.88; N, 3.63%.

### 2.3.5. $[Fe(O_2CAr^{Tol})_2(BPTA)]$ (7)

To a rapidly stirred CH<sub>2</sub>Cl<sub>2</sub> (2 ml) solution of 1 (102 mg, 69.8 µmol) was added dropwise BPTA (36 mg, 0.14 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 ml). The intense yellow solution was stirred for 15 min and volatile fractions were removed under reduced pressure. The residual orange solid was extracted into PhCl (2 ml) and insoluble material was filtered off. Vapor diffusion of pentanes into the yellow filtrate afforded yellow needles of 7 (102 mg, 0.111 mmol, 80%), which were suitable for X-ray crystallography. FT-IR (KBr,  $cm^{-1}$ ) 3053(m), 3024(m), 2974(m), 2919(m), 1623(vs), 1606(vs), 1576(s), 1515(vs), 1477(s), 1442(vs), 1404(s), 1372(s), 1354(vs), 1189(w), 1149(w), 1021(m), 833(m), 799(s), 767(vs), 701(m), 532(m); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>) ( $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)) 433 (1300). Anal. Calc. for  $C_{58}H_{55}FeN_3O_4$ . C<sub>6</sub>H<sub>5</sub>Cl: C, 74.89; H, 5.89; N, 4.09. Found: C, 75.00; H, 6.20; N, 4.14%.

#### 2.4. X-ray crystallography

Intensity data were collected on a Bruker (formerly Siemens) CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), controlled by a Pentium-based PC running the SMART software package [28]. Single crystals were mounted at r.t. on the tips of quartz fibers, coated with Paratone-N oil, and cooled to 188 K under a stream of cold nitrogen maintained by a Bruker LT-2A nitrogen cryostat. Data collection and reduction protocols are described elsewhere [29]. The structures were solved by direct methods and refined on  $F^2$  by using the SHELXTL software package [30]. Empirical absorption corrections were applied with SADABS [31], part of the SHELXTL program package, and the structures were checked for higher symmetry by the program PLATON [32]. All non-hydrogen atoms were refined anisotropically unless otherwise noted. Hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to either 1.5 (methyl hydrogen atoms) or 1.2 (all other hydrogen atoms)

Table 1	
Summary of X-ray	crystallographic data

	3	4	5.2MeCN	6	7 · PhCl
Empirical formula	C <sub>62</sub> H <sub>54</sub> FeN <sub>4</sub> O <sub>4</sub>	C <sub>58</sub> H <sub>50</sub> FeN <sub>4</sub> O <sub>4</sub>	C <sub>68</sub> H <sub>72</sub> FeN <sub>4</sub> O <sub>4</sub>	C48H50FeN2O4	C <sub>64</sub> H <sub>59</sub> ClFeN <sub>3</sub> O <sub>4</sub>
Formula weight	974.9	922.9	1065.2	774.8	1025.4
Temperature (°C)	-85	-85	-85	-85	-85
Space group	$P\overline{1}$	C2/c	$P\overline{1}$	$P2_1/n$	$P\overline{1}$
a (Å)	12.7648(4)	14.453(17)	14.1779(12)	12.4478(4)	13.3303(4)
b (Å)	14.5563(5)	23.21(2)	14.4349(13)	19.9561(6)	16.6989(4)
c (Å)	15.4066(6)	15.667(10)	14.7856(13)	17.2865(5)	26.8209(6)
α (°)	73.8100(10)		78.700(3)		99.7700(10)
β (°)	67.795(2)	114.03(5)	84.547(2)	110.7520(10)	102.9470(10)
γ (°)	84.0580(10)		83.7120(10)		104.31
V (Å <sup>3</sup> )	2545.26(15)	4800(8)	2941.0(4)	4015.5(2)	5475.4(2)
Ζ	2	4	2	4	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.272	1.277	1.203	1.282	1.244
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.349	0.366	0.308	0.423	0.375
$\theta$ Limits (°)	1.81 - 28.30	1.75-28.29	1.94-28.34	1.62-28.31	1.61 - 28.30
Total no. of data	16198	4892	18565	24856	34765
No. of unique data	11287	3479	12990	9231	24237
No. of parameters	640	310	690	522	1333
$R (\%)^{\bar{a}}$	6.80	3.80	6.21	4.06	7.03
$wR_2$ (%) <sup>b</sup>	11.10	9.40	14.23	9.27	12.10
Max, min peaks (e $Å^{-3}$ )	0.310, -0.341	0.197, -0.225	0.445, -0.339	0.355, -0.413	0.291, -0.328

<sup>a</sup>  $R = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|.$ 

<sup>b</sup> 
$$wR^2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

times the thermal parameter of the carbon atom to which they were attached. The hydrogen atoms associated with the disordered solvent molecules were not included in the refinement. The butyl groups on one of the  $\operatorname{Ar}^{4-t\operatorname{BuPh}}\operatorname{CO}_2^{-}$  ligands in **5** were disordered over two positions. The atoms were equally distributed and refined isotropically. The disordered ethylene carbon atoms of the TMEDA ligand in **6** were equally distributed over two positions and refined isotropically. Each of the chlorine atoms associated with the two PhCl solvent molecules in the structure of **7** were disordered over two positions. One was refined at 0.7 and 0.3 occupancy; the other refined to 0.6 and 0.4. Crystallographic information is provided in Table 1.

#### 3. Results

3.1. Synthesis, and structural characterization of  $[Fe(O_2CAr^{Tol})_2(1-BnIm)_2]$  (3),  $[Fe(O_2CAr^{Tol})_2(1-MeBzIm)_2]$  (4),  $[Fe(O_2CAr^{4-tBuPh})_2(2,2'-bipy)]$  (5),  $[Fe(O_2CAr^{Tol})_2(TMEDA)]$  (6), and  $[Fe(O_2CAr^{Tol})_2(BPTA)]$  (7)

Compound **3** was prepared from a reaction between **1** and 1-BnIm in  $CH_2Cl_2$ . Even when a 2:1 ratio of 1-BnIm to **1** was used, only a mononuclear complex was isolated, which incorporated two N-donor ligands per iron(II). The preparation was thus optimized by using >4 equiv of 1-BnIm per **1**, which afforded colorless blocks of **3** in good yield (78%). The crystal structure of

**3** is shown in Fig. 1; selected bond lengths and angles are listed in Table 2. The pseudo-tetrahedral iron center in **3** is coordinated by two monodentate carboxylate and two 1-BnIm ligands. The metrical parameters are normal for high-spin iron(II) centers and comparable to those of related compounds [Fe(O<sub>2</sub>CAr<sup>Mes</sup>)<sub>2</sub>L<sub>2</sub>] (L = 1-MeIm or pyridine) built on sterically more demanding carboxylate ligands, 2,6-di(mesityl)benzoate (Ar<sup>Mes</sup>CO<sub>2</sub><sup>-</sup>) [33].

When a similar procedure was used for 1 and 1-MeBzIm, a six-coordinate mononuclear complex 4 was isolated following recrystallization from MeOH-MeCN-Et<sub>2</sub>O. The crystal structure of **4** is shown in Fig. 1; selected bond lengths and angles are listed in Table 2. A crystallographic  $C_2$ -symmetry bisects the molecule and two symmetry-related bidentate carboxylate and 1-MeBzIm ligands support a highly distorted octahedral iron center. The binding of the carboxylate ligands is asymmetric, as reflected in the two distinct Fe–O distances with  $\Delta_{\text{Fe–O}} \sim 0.31$  Å (Table 2). The longer Fe-O bond is positioned trans to the N-donor atoms and the average Fe–O distance of  $\sim 2.23$  Å is significantly longer than that (  $\sim 1.99$  Å) in 3. Despite an increase in coordination number, however, the N-Fe-N angle of  $114.99(12)^{\circ}$  in **4** is significantly larger than that in 3, presumably due to the steric interaction between cis-coordinated bulky N-donor ligands. Much smaller N-Fe-N angles of 90.3(1)-97.6(2)° were obtained for related six-coordinate iron(II) complexes [Fe(O<sub>2</sub>CAr<sup>Mes</sup>)<sub>2</sub>L<sub>2</sub>] having sterically less demanding ligands such as 2-picoline or 2,5-lutidine [33].



Fig. 1. ORTEP diagrams of  $[Fe(O_2CAr^{Tol})_2(1-BnIm)_2]$  (3) (left) and  $[Fe(O_2CAr^{Tol})_2(1-MeBzIm)_2]$  (4) (right) with thermal ellipsoids at 50% probability.

Ligand substitution reactions of 1 with bidentate imine or amine donors afforded five-coordinate iron(II) complexes 5 and 6 having N<sub>2</sub>O<sub>3</sub> donor atom sets. When a CH<sub>2</sub>Cl<sub>2</sub> solution of 1 was treated with 2 equiv of 2,2'bipy, the color of the solution turned bluish purple and a highly intractable solid material deposited immediately. In order to enhance the solubility of this 2,2'-bipy adduct(s), the less polar Ar<sup>4-tBuPh</sup>CO<sub>2</sub><sup>-</sup> ligand was used to replace  $Ar^{Tol}CO_2^{-}$ . Compound 5 was isolated in modest yield ( $\sim 56\%$ ) from a reaction between Fe(OTf)<sub>2</sub>·2MeCN, NaO<sub>2</sub>CAr<sup>4-tBuPh</sup>, and 2,2'-bipy in a 1:2:1 ratio in MeCN. The use of the polar solvent MeCN apparently facilitates isolation of the neutral product 5, which precipitates directly from the reaction mixture in analytically pure, crystalline form. The crystal structure of 5 is shown in Fig. 2; selected bond lengths and angles are available in Table 2. Compound 5 has one bidentate and one monodentate carboxylate ligands. The symmetric bonding a bidentate carboxylate  $(\Delta_{\text{Fe}-\text{O}} \cong 0.023 \text{ Å})$  has Fe–O distances of 2.194(2) and 2.171(2) Å, which are significantly longer than that of the monodentate carboxylate, 2.015(2) Å.

Compound **6** can be prepared either by ligand substitution of **1** with 2 equiv of TMEDA or by direct self-assembly from Fe(OTf)<sub>2</sub>·2MeCN, NaO<sub>2</sub>CAr<sup>Tol</sup>, and TMEDA in a 1:2:1 ratio in THF. Colorless blocks were obtained in excellent yield (80-91%) following recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-pentanes-hexanes. The crystal structure of **6** is shown in Fig. 2; selected bond lengths and angles are available in Table 2. The highly distorted trigonal bipyramidal iron atom (O(1A)-Fe(1)-O(1B) = 157.80(6)°) is coordinated by one bidentate and one monodentate carboxylate, as in **5**. The flexible ethylene linker between the two N-donor atoms affords a slightly expanded N-Fe-N angle of 82.66(6)° compared with the 75.57(11)° value in **5**. Unlike **5**, however, binding of  $\eta^2$ -carboxylate in **6** is highly asymmetric ( $\Delta_{\text{Fe}-\text{O}} \cong 0.289$  Å), with a longer Fe(1)– O(2A) bond positioned trans to the amine donors.

Reaction of 1 with 2 equiv of BPTA in CH<sub>2</sub>Cl<sub>2</sub> afforded yellow needles of 7 in good yield (80%). The crystal structure of 7 is shown in Fig. 3; selected bond lengths and angles are available in Table 2. X-ray structure analysis revealed two chemically identical but crystallographically inequivalent molecules in the unit cell. The tridentate BPTA ligand binds in a meridional configuration, positioning the two pyridine nitrogen atoms at the pseudoaxial sites of a distorted trigonal bipyramidal. The N(1P)-Fe(1)-N(1Q) angles are 152.28(18) and 153.09(18)°. A pair of monodentate carboxylates and a tertiary amine complete the N<sub>3</sub>O<sub>2</sub> donor atom set. The Fe-N<sub>pyridine</sub> distances of 2.100(4) to 2.137(4) Å in 7 are comparable to the Fe-N<sub>imidazole/pyridine</sub> distances of 2.074(4)-2.141(3) Å in 3-5, but significantly shorter than the Fe-N<sub>amine</sub> distances of 2.336(4)-2.353(4) Å. A similar trend was observed for dimanganese(III) and dimanganese(IV) complexes supported by BPTA [26]. Compound 7 displays an intense  $(\varepsilon = 1300 \text{ M}^{-1} \text{ cm}^{-1})$  visible band at  $\lambda_{\text{max}} = 433 \text{ nm}$ , assigned as a MLCT transition. Similar transitions occur at  $\sim 360$  nm in related complexes having comparable  $\varepsilon$  values per iron(II)-pyridine unit (500–1000 M<sup>-1</sup>  $cm^{-1}$ ) [34].

#### 3.2. Mössbauer spectroscopy

Zero-field Mössbauer spectra (Figs. 4 and 5) of solid samples of 2-5 and 7 were collected at 4.2 K. The corresponding parameters derived from fits of the spectra are provided in Table 3 along with those of related diiron(II) complexes. Consistent with the presence of two distinct iron(II) centers in the dinuclear

Table 2 Selected bond lengths (Å) and angles (°) for 3, 4, 5  $\cdot$  2MeCN, 6, and 7  $\cdot$  PhCl <sup>a</sup>

Bond lengths		Bond angles	
$\frac{1}{3}$ Fe(1)-O(1) Fe(1)-O(3) Fe(1)-N(1) Fe(1)-N(3) 4	1.989(3) 1.996(3) 2.074(4) 2.121(4)	$\begin{array}{c} O(1)-Fe(1)-O(3)\\ O(1)-Fe(1)-N(1)\\ O(3)-Fe(1)-N(1)\\ O(1)-Fe(1)-N(3)\\ O(3)-Fe(1)-N(3)\\ N(1)-Fe(1)-N(3) \end{array}$	147.58(13) 107.68(14) 95.25(14) 90.13(14) 109.02(14) 98.89(15)
Fe(1)–O(1) Fe(1)–O(2) Fe(1)–N(1)	2.076(3) 2.384(2) 2.128(2)	$\begin{array}{l} O(1)-Fe(1)-O(1A)\\ O(1)-Fe(1)-N(1)\\ O(1)-Fe(1)-N(1A)\\ O(1)-Fe(1)-O(2)\\ O(1)-Fe(1)-O(2A)\\ N(1)-Fe(1)-O(2A)\\ N(1)-Fe(1)-O(2A)\\ O(2)-Fe(1)-O(2A)\\ N(1)-Fe(1)-N(1A) \end{array}$	156.77(1) 107.93(8) 84.75(8) 58.58(7) 102.22(8) 93.72(9) 139.58(7) 79.51(11) 114.99(12)
5.2MeCN Fe(1)-O(1A) Fe(1)-O(2A) Fe(1)-O(1B) Fe(1)-N(1) Fe(1)-N(2)	2.194(2) 2.171(2) 2.015(2) 2.131(3) 2.141(3)	$\begin{array}{l} O(1A)-Fe(1)-O(2A)\\ O(1A)-Fe(1)-O(1B)\\ O(1B)-Fe(1)-N(1)\\ O(1B)-Fe(1)-N(2)\\ O(1B)-Fe(1)-O(2A)\\ N(1)-Fe(1)-O(2A)\\ N(2)-Fe(1)-O(2A)\\ N(1)-Fe(1)-O(1A)\\ N(2)-Fe(1)-O(1A)\\ N(1)-Fe(1)-N(2)\\ \end{array}$	60.08(9) 100.92(9) 141.94(11) 112.81(10) 101.80(10) 112.95(10) 101.85(10) 84.19(10) 144.82(10) 75.57(11)
6 Fe(1)-O(1A) Fe(1)-O(2A) Fe(1)-O(1B) Fe(1)-N(1) Fe(1)-N(2)	2.0641(14) 2.3527(14) 1.9590(13) 2.1868(16) 2.2119(16)	$\begin{array}{l} O(1A)-Fe(1)-O(1B)\\ O(1A)-Fe(1)-O(2A)\\ O(1B)-Fe(1)-O(2A)\\ O(1A)-Fe(1)-N(1)\\ O(1A)-Fe(1)-N(2)\\ O(1B)-Fe(1)-N(1)\\ O(1B)-Fe(1)-N(2)\\ N(1)-Fe(1)-O(2A)\\ N(2)-Fe(1)-O(2A)\\ N(1)-Fe(1)-N(2) \end{array}$	$\begin{array}{c} 157.80(6)\\ 59.07(5)\\ 104.11(5)\\ 103.28(6)\\ 91.06(6)\\ 96.89(6)\\ 100.73(6)\\ 114.16(6)\\ 147.65(6)\\ 82.66(6) \end{array}$
7 · PhCl Fe(1)-O(1A) Fe(1)-O(1B) Fe(1)-N(1Q) Fe(1)-N(1P) Fe(1)-N(01)	2.116(3) <sup>b</sup> 2.150(3) <sup>c</sup> 2.007(3) <sup>b</sup> 1.995(3) <sup>c</sup> 2.121(4) <sup>b</sup> 2.100(4) <sup>c</sup> 2.137(4) <sup>b</sup> 2.122(4) <sup>c</sup> 2.336(4) <sup>c</sup>	O1A-Fe1-O1B O1A-Fe1-N1P O1A-Fe1-N1Q O1A-Fe1-N01 O1B-Fe1-N1P O1B-Fe1-N1Q O1B-Fe1-N01 N1P-Fe1-N01 N1P-Fe1-N01	$\begin{array}{c} 87.80(14) \\ 91.68(13) \\ c \\ 91.68(13) \\ c \\ 98.98(15) \\ c \\ 96.72(14) \\ b \\ 96.74(15) \\ c \\ 142.17(14) \\ c \\ 142.12(13) \\ c \\ 91.92(15) \\ b \\ 93.50(14) \\ c \\ 109.69(14) \\ b \\ 107.76(15) \\ c \\ 129.76(13) \\ b \\ 125.96(13) \\ c \\ 153.09(18) \\ c \\ 76.28(15) \\ b \\ 77.25(17) \\ c \\ 76.53(15) \\ b \end{array}$

<sup>&</sup>lt;sup>a</sup> Numbers in parentheses are estimated standard deviations of the last significant figures. Atoms are labeled as indicated in Figs. 1–3.

<sup>c</sup> Molecule 2.

unit, **2** exhibits two overlapping doublets with equal intensities. Compounds 3–5 and 7 display single sharp ( $\Gamma = 0.24-0.31$  mm s<sup>-1</sup>) quadrupole doublets. The isomer shifts and quadrupole splittings of these compounds are typical of high-spin iron(II) sites in a N/O coordination environment [35–37] and comparable to those obtained for related diiron(II) complexes (Table 3) [20].

#### 4. Discussion

#### 4.1. Synthesis of iron(II) carboxylate complexes

Synthetic routes to the Ar<sup>Tol</sup>CO<sub>2</sub><sup>-</sup>-supported iron(II) complexes developed in this and previous investigations are summarized in Scheme 1. The iron(II) centers in these compounds are nestled within the hydrophobic cavity afforded by the *p*-substituted aryl groups flanking the carboxylate unit on  $Ar'CO_2^-$  ( $Ar' = Ar^{Tol}$  or Ar<sup>4-tBuPh</sup>). This steric shield attenuates the tendenacy of kinetically labile iron-carboxylate units to assemble into higher nuclearity species [38]. The nuclearity and coordination geometry of these compounds are apparently dictated by the electronic and steric properties of the N-donor ligands. Structural diversity within the  $[Fe(O_2CAr^{Tol})_2L_2]$  modules is further extended by the flexible coordination of the carboxylate ligands, which translates into distinctive Mössbauer parameters obtained for these compounds (vide infra).

# 4.1.1. Dimetallic core disassembly upon ligand substitution with monodentate N-donors

Minimal structural perturbation is introduced into the carboxylate-bridged diiron(II) core of 1 upon displacement of the weakly bound THF ligands by MeCN, pyridine, or 1-methylimidazole [12,20]. Binding of sterically more demanding monodentate N-donor ligands such as 1-BnIm or 1-MeBzIm, however, dissociates the dinuclear core into mononuclear iron(II) dicarboxylate complexes 3 or 4. Members of this rare class of iron(II) compounds having two carboxylate and two N-donor ligands were previously prepared by using a dinucleating dicarboxylate XDK [10] or a *m*-terphe- $Ar^{Mes}CO_2^{-}$ nvl-derived ligand. In [Fe(u-XDK (C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> (A), the iron atom is coordinated by three carboxylate oxygen and two pyridine nitrogen atoms [34]. Four- or six-coordinate iron(II) centers can be stabilized within the  $[Fe(O_2CAr^{Mes})_2L_2]$  platform Related mononuclear iron(II) complexes [33].  $[Fe(OAc)_2(C_5H_5N)_4]$  (B) and  $[Fe(OAc)_3(C_5H_5N)]^-$  (C) can be prepared by chemical reduction of a basic iron acetate cluster [Fe<sub>3</sub>O(OAc)<sub>6</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>3</sub>] in a mixture of pyridine and AcOH [39,40]. Without an effective steric shield or conformational rigidity, however, these com-

<sup>&</sup>lt;sup>b</sup> Molecule 1.



Fig. 2. ORTEP diagrams of  $[Fe(O_2CAr^{4-tBuPh})_2(2,2'-bipy)]$  (5) (left) and  $[Fe(O_2CAr^{Tol})_2(TMEDA)]$  (6) (right) with thermal ellipsoids at 50% probability.



Fig. 3. ORTEP diagram of  $[Fe(O_2CAr^{Tol})_2(BPTA)]$  (7) with thermal ellipsoids at 50% probability.

pounds exist in equilibrium with higher nuclearity species in solution.

The shift in the coordination number from fourcoordinate in 3 to six-coordinate in 4 results from a change in the carboxylate denticity and correlates with the electron density at the metal center. Coordination of the less electron-donating ligand 1-MeBzIm ( $pK_a = 5.7$ ) compared to 1-BnIm ( $pK_a = 6.7$ ) [41,42] enhances the Lewis acidity at the metal center, inducing a carboxylate shift from monodentate to bidentate chelating. A recent structural analysis of iron(II) complexes [Fe(O<sub>2</sub>-CAr<sup>Mes</sup>)<sub>2</sub>L<sub>2</sub>] (L = N-donor ligands) [33] supports this notion.

#### *4.1.2. Effects of conformationally restricted bidentate Ndonors*

The five-coordinate complexes **5** and **6** are favored when 2,2'-bipy and TMEDA, respectively, are employed. Although an identical N<sub>2</sub>O<sub>3</sub> donor atom set occurs in **5** and **6**, the bidentate ligands in these complexes have significantly different donor abilities, as indicated by the  $pK_a$  values of 4.3 for 2,2'-bipy [43] and 9.0 for TMEDA [44]. Both the electronic and steric properties of the ligands in **6** suggest that it, like **3**, might adopt a four-coordinate geometry due to the enhanced donor ability of the amine groups as well as the steric crowding induced by four methyl groups on TMEDA. Compound **5**, on the other hand, might favor sixcoordination, since 2,2'-bipy has a  $pK_a$  value even lower





Fig. 4. Zero-field Mössbauer spectra (experimental data (|), calculated fit(–)) recorded at 4.2 K for a solid sample of  $[Fe_2(\mu-O_2CAr^{Tol})_3(O_2-CAr^{Tol})(2,6-lutidine)]$  (2). The upper curves show two subsets for the calculated spectra. See Table 3 for derived Mössbauer parameters.

than that (5.7) of 1-MeBzIm. The solid state structures of **5** and **6**, however, indicate the failure of these simple arguments to predict the correct geometry, since both are five-coordinate. The bidentate ligands 2,2'-bipy and TMEDA afford smaller N-Fe-N bite angles (75.6– 82.7°) than that (98.9°) in **3**, promoting coordination numbers higher than four. They are conformationally restrictive, however, and may not allow the structural rearrangement required to alleviate steric crowding in six-coordination.

Recent DFT calculations of  $[Zn(OAc)_x(Im)_yL_z]^{n+}$ models revealed an energetically very flat potential surface of carboxylate coordination, which allows barrierless interconversion between different carboxylate binding modes [45]. If similar isoenergetic processes are operative for the  $[Fe(O_2CAr^{Tol})_2L_n]$  module, the correlation between electronic and stereochemical properties becomes less than straightforward.

#### 4.1.3. Flexible tridentate N-donor ligand

Binding of the three nitrogen atoms of BPTA afforded the five-coordinate iron(II) complex 7, which has two monodentate carboxylate ligands. Amine/imine mixed-donor ligands derived from the N,N-bis(2-pyr-idylmethyl)amine (BPA) module have been extensively employed to stabilize biomimetic polymanganese clus-



Fig. 5. Zero-field Mössbauer spectra (experimental data (]), calculated fit(–)) recorded at 4.2 K for solid samples of  $[Fe(O_2CAr^{Tol})_2(1-BnIm)_2]$ (3) (A);  $[Fe(O_2CAr^{Tol})_2(1-MeBzIm)_2]$  (4) (B);  $[Fe(O_2CAr^{4-tBuPh})_2(2,2'-bipy)]$  (5); (C)  $[Fe(O_2CAr^{Tol})_2(BPTA)]$  (7). See Table 3 for derived Mössbauer parameters.

ters [26,46–48]. Unlike TACN- or [HBpz]<sub>3</sub>-derived tridentate ligands [10], conformationally flexible BPA analogs allow both facial and meridional coordination [47,49]. This feature prompted us to investigate the structural properties of its iron(II) complexes. In order to prevent the formation of unwanted bis(chelate)

Table 3

4.2 K zero-field Mössbauer parameters for  $[Fe_2(\mu-O_2CAr^{Tol})_3(O_2CAr^{Tol})(2,6-lutidine)]$  (2),  $[Fe(\mu-O_2CAr^{Tol})_2(1-BnIm)_2]$  (3),  $[Fe(O_2CAr^{Tol})_2(1-MeBzIm)_2]$  (4),  $[Fe(O_2CAr^{4-tBuPh})_2(2,2'-bipy)]$  (5),  $[Fe(O_2CAr^{Tol})_2(BPTA)]$  (7), and related diiron(II) complexes

Compound	$\delta \ ({\rm mm} \ {\rm s}^{-1})$	$\Delta E_{\rm Q} \ ({\rm mm} \ {\rm s}^{-1})$	$\Gamma_{\rm L} ({\rm mm}{\rm s}^{-1})$	$\Gamma_{\rm R} \ ({\rm mm} \ {\rm s}^{-1})$		Coordination number	Reference
2	1.05(2)	2.18(2)	0.31	0.31	site 1	4	This work
	1.23(2)	2.80(2)	0.28	0.28	site 2	5	
3	1.08(2)	2.46(2)	0.26	0.31		4	This work
4	1.16(2)	2.82(2)	0.24	0.26		6	This work
5	1.13(2)	2.91(2)	0.29	0.28		5	This work
7	1.10(2)	3.52(2)	0.26	0.26		5	This work
$[Fe_2(\mu-O_2CAr^{Tol})_2(O_2CAr^{Tol})_2(THF)_2]$	1.26(2)	2.90(2)	0.27	0.28		5 <sup>a</sup>	[20]
$[Fe_{2}(\mu-O_{2}CAr^{Tol})_{2}(O_{2}CAr^{Tol})_{2}(C_{5}H_{5}N)_{2}]$	1.19(2)	3.02(2)	0.25	0.25		5 <sup>a</sup>	[20]

<sup>a</sup> Two iron atoms are equivalent.

compounds [Fe(BPA)<sub>2</sub>]X<sub>2</sub> [50], a *tert*-butyl group was installed on the amine nitrogen atom. As shown in Fig. 3, meridional coordination of BPTA provides a pair of *cis* oriented coordination sites for carboxylate binding. Monodentate coordination of the carboxylate ligands alleviates steric crowding between the  $Ar^{Tol}CO_2^{-1}$  ligands and *tert*-butyl group on BPTA. Carboxylate shifts [51] thus allow both N<sub>2</sub>O<sub>3</sub> and N<sub>3</sub>O<sub>2</sub> donor combinations without a change in overall coordination number for 5–7.

#### 4.2. Mössbauer spectroscopy

Mössbauer spectroscopy is an excellent method for establishing the oxidation and spin states of iron atoms [35]. Among biologically relevant oxidation and spin states, only high-spin (S = 2) iron(II) has a unique range of isomer shift ( $\delta$ ) values [36,37]. The coordination environment and degree of metal-ligand covalency can be deduced from the quadrupole splitting parameter,  $\Delta E_Q$ , which reflects the electric field gradient (EFG) generated by the charges surrounding the iron site. Mössbauer parameters obtained for well-defined iron carboxylate complexes thus can be used to aid the assignment of spectra for structurally related biological iron clusters. Even for structurally characterized iron model compounds, however, an assignment of quadruple doublets to individual subsites can be ambiguous when multiple asymmetric iron(II) centers occur within a given molecule [34,52,53]. We therefore investigated



Scheme 1.

the Mössbauer parameters of the mononuclear iron(II) complexes prepared here as subsite models that can be used to deconvolute more complicated spectra obtained for structurally related polyiron clusters.

Compound 2 is one such species, in which there are two distinct iron sites, Fe(1) (four-coordinate) and Fe(2) (five-coordinate), within the dinuclear unit. The asymmetric coordination environment of the two iron atoms in 2 results in two overlapping quadrupole doublets displayed in the 4.2 K zero-field Mössbauer spectra (Fig. 4). Valence bond theory dictates that the lower-coordinate Fe(1) site should have greater s-character relative to Fe(2) and a negatively shifted  $\delta$  value. The quadrupole doublet having the small isomer shift of 1.05 mm s<sup>-1</sup> is therefore assigned to Fe(1) and the one with the larger isomer shift of 1.23 mm s<sup>-1</sup> to Fe(2). This assignment requires that the smaller  $\Delta E_Q$  value (2.18 mm s<sup>-1</sup>) belongs to Fe(1), which indeed displays a more symmetric tetrahedral coordination sphere. Consistent with this analysis is the observation that, in the fourcoordinate complex 3, the  $\delta$  and  $\Delta E_Q$  values lie at the low end of the range ( $\delta = 1.08 - 1.16 \text{ mm s}^{-1}$ ;  $\Delta E_Q =$ 2.46–3.52 mm s<sup>-1</sup>) of parameters for  $[Fe(O_2CAr')_2L_n]$ compounds (Table 3). The subspectrum of 2 displaying the larger  $\Delta E_Q$  value (2.80 mm s<sup>-1</sup>) is assigned to the more asymmetric, highly distorted five-coordinate atom Fe(2). Comparable quadrupole splittings (2.90-3.02 mm s<sup>-1</sup>) were obtained for 1 and  $[Fe_2(\mu-O_2CAr^{Tol})_2-(O_2CAr^{Tol})_2(C_5H_5N)_2]$  [12], in which analogous fivecoordinate iron(II) centers are coordinated by  $O_5$  and NO<sub>4</sub> donor sets, respectively. Deviations from a perfectly symmetric distribution of donor atoms are reflected in similarly large  $\Delta E_Q$  values of 2.82-3.52 mm  $s^{-1}$  exhibited by 4, 5, and 7.

As summarized in Table 3, a distribution of  $\Delta E_Q$  values occurs for the [Fe(O<sub>2</sub>CAr')<sub>2</sub>L<sub>2</sub>] series of compounds. Asymmetry in coordination geometry as well as the positioning of different donor atoms apparently reinforce the intrinsic EFG of high-spin iron(II). A rigorous correlation between the Mössbauer parameters and overall stereochemistry of the iron(II) complexes cannot be made, however, in part owing to the limited number of well-defined basis sets available. Analysis of the Mössbauer data of **2** as described above, however, clearly demonstrates that mononuclear complexes can serve as effective subsite models for higher nuclearity species. It remains to be seen whether such an approach is generally applicable to a larger number of examples sharing similar architectural features.

#### 5. Summary and conclusions

A series of mononuclear iron(II) complexes were obtained from a common diiron(II) precursor complex. Sterically demanding *m*-terphenyl-derived carboxylate ligands stabilize four-, five-, and six-coordinate complexes having rare coordination geometries. Structural variations within the  $[Fe(O_2CAr')_2L_n]$  module are dictated by the steric and electronic properties of the N-donor ligands and accommodated by flexible coordination of the carboxylate ligands. Mössbauer parameters obtained for these compounds were used to assist spectral assignment of a dinuclear complex. Structurally related mononuclear complexes thus may serve as useful subsite models for higher nuclearity species in both synthetic and biological systems.

#### 6. Supplementary material

Full tables of crystallographic parameters and structure refinement, positional and isotropic thermal parameters, bond distances, bond angles, and components of the anisotropic thermal parameters have been deposited with the Cambridge Data Centre, CCDC Nos. 192206– 192209 (for 3–5 and 7). Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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- [10] Abbreviations used: Ar<sup>Mes</sup>, 2,6-dimesitylphenyl; XDK, m-xylenediamine bis(Kemp's triacid imide); TACN, 1,4,7-triazacyclononane; [HBpz]<sub>3</sub>, hydrotris(1-pyrazolyl)borate.
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