

Synthesis, structures of mononuclear and dinuclear iron(II) complexes supported by non-symmetric guanidinate(amidinate) ligands

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ABSTRACT

A new family of Fe(II) compounds, **1–3**, have been prepared, which are derived from the non-symmetric lithium guanidinate Li(**L**₁) [**L**₁ = N(Ph)C(R)N(SiMe₃)] (R = 1-piperidino) or the lithium amidinates Li(**L**₂) [**L**₂ = N(Ph)C(Ph)N(SiMe₃)] or Li(**L**₃) [**L**₃ = N(2,6-*i*-Pr₂C₆H₃)C(Ph)N(SiMe₃)]. Treatment of Li(**L**₁), Li(**L**₂) or Li(**L**₃) with anhydrous FeCl₂ afforded [(**L**₁)₄Fe₂] (**1**), [(**L**₂)₄Fe₂] (**2**) or [(**L**₃)₂Fe] (**3**), respectively. The molecular structures of **1–3** were determined by an X-ray diffraction study.

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1. Introduction

The guanidinate and related amidinate ligands have been largely explored and remain of special interest because of their great potential in ligand design [1–8]. The tunable nature of the steric and electronic parameters is one of the distinctive traits of these ligands. In addition, the ligands can display a variety of bonding modes to metals.

In some binuclear guanidinate(amidinate) metal complexes, the ligands bind two metal ions in an unusual bridging coordination mode, e.g. ladder structures for binuclear lithium amidinates [9–12]; $\mu, \eta^1: \eta^1-$, $\mu, \eta^2: \eta^2-$, $\mu, \eta^2: \eta^1$ -structures for binuclear Fe(II), Co(II), Pd, Mg, Ca, Sr guanidinate(amidinate) compounds [13–20] and rare *N,N'*-(TMEDA)-bridging in binuclear Mn(II) and Co(II) amidinates [21].

Currently, we are interested in the chemistry of metal complexes supported by non-symmetric guanidinate(amidinate) ligands [22,23]. These ligands were prepared via the nucleophilic reactions of *N*-centered anions to nitriles free from α -hydrogen atoms, migrations of SiMe₃ and isomerization. They have been shown to be versatile in supporting a number of main group and transition metal complexes. Herein we report the preparation and molecular structures of a series of new Fe(II) complexes derived from Li(**L**₁) [**L**₁ = N(Ph)C(R)N(SiMe₃)] (R = 1-piperidino), Li(**L**₂) [**L**₂ = N(Ph)C(Ph)N(SiMe₃)] or Li(**L**₃) [**L**₃ = N(2,6-*i*-Pr₂C₆H₃)C(Ph)N(SiMe₃)], namely the binuclear Fe(II) guanidinate(amidinate)

complexes [**L**₄Fe₂] (**L** = **L**₁, **1**; **L**₂, **2**) and the mononuclear Fe(II) amidinate compound [(**L**₃)₂Fe] (**3**). Furthermore, the effect of the nitrogen atom substituents on the structures of the resulting Fe(II) complexes **1–3** is discussed.

2. Results and discussion

2.1. Synthesis and characterization

Complexes **1–3** were readily prepared by treating Li(**L**₁), Li(**L**₂) or Li(**L**₃) with iron(II) chloride (Scheme 1). The binuclear Fe(II) guanidinate(amidinate) complexes [(**L**₁)₄Fe₂] (**1**) and [(**L**₂)₄Fe₂] (**2**), isolated as yellow crystals, were synthesized by treating anhydrous FeCl₂ with two equivalents of Li(**L**₁) or Li(**L**₂) in diethyl ether. A similar reaction of anhydrous FeCl₂ with Li(**L**₃) afforded yellow crystals of mononuclear [(**L**₃)₂Fe] (**3**).

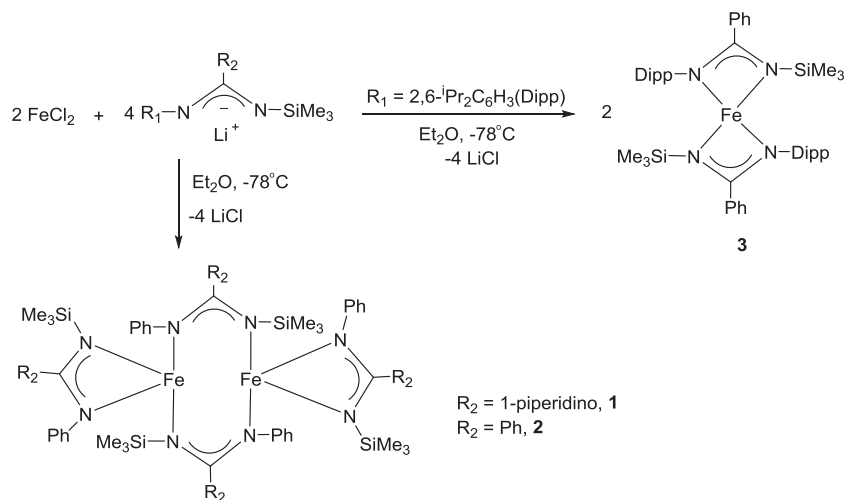
Suitable crystals for X-ray diffraction studies of **1–3** were obtained from the saturated diethyl ether solution at low temperature. The air-sensitive **1** changed into a dark-red powder in 2 h, whereas **2** and **3**, when in contact with air, turned into yellow powders in 5 and 20 min, respectively. Complexes **1–3** are readily soluble in Et₂O, THF and toluene. They are paramagnetic species. The elemental analyses results are consistent with the calculated values.

2.2. Crystal structures of **1–3**

Complexes **1** and **2** are dimeric and isostructural. The iron atoms in both **1** (Fig. 1) and **2** (Fig. 2) are located in a slightly

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Scheme 1. Synthesis of 1–3.

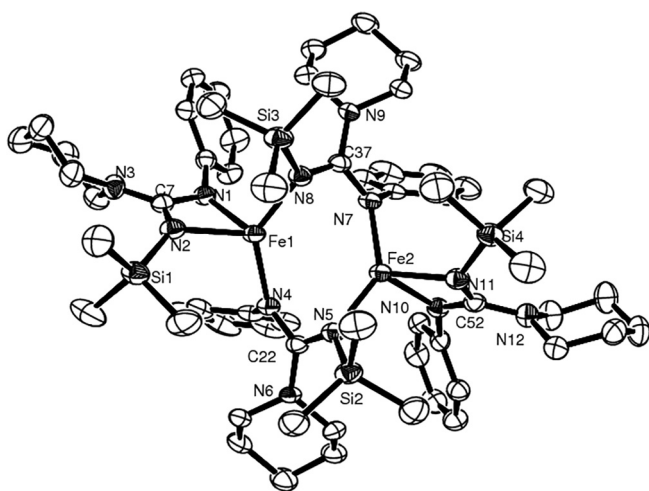


Fig. 1. Perspective ORTEP drawing of the molecular structure of **1**. All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 50% probability. Selected bond lengths (Å) and angles (deg): Fe(1)–N(1) 2.103(3), Fe(1)–N(2) 2.140(3), Fe(1)–N(4) 2.028(2), Fe(1)–N(8) 2.026(3), Fe(2)–N(5) 2.024(2), Fe(2)–N(7) 2.028(2), Fe(2)–N(10) 2.112(2), Fe(2)–N(11) 2.121(3), N(1)–C(7) 1.342(4), N(2)–C(7) 1.349(4), N(4)–C(22) 1.353(4), N(5)–C(22) 1.342(4), N(7)–C(37) 1.351(4), N(8)–C(37) 1.348(4), N(10)–C(52) 1.335(4), N(11)–C(52) 1.351(4); N(1)–Fe(1)–N(2) 63.86(9), N(4)–Fe(1)–N(8) 133.53(10), N(10)–Fe(2)–N(11) 64.07(9), N(5)–Fe(2)–N(7) 135.96(10), N(1)–C(7)–N(2) 113.0(3), N(4)–C(22)–N(5) 119.3(3), N(7)–C(37)–N(8) 120.1(3), N(10)–C(52)–N(11) 113.5(3).

distorted tetrahedral environment, in which each iron atom is bonded to the N atoms of one guanidinate(amidinate) ligand in a terminal, chelating η^2 -fashion and to the N atoms of two guanidinate(amidinate) ligands with μ_2 -interaction. For the η^2 -fashion section, the Fe–N bond lengths are in the range 2.103(3)–2.140(3) Å in **1** and 2.110(2)–2.126(2) Å in **2**. They are longer than those of the μ_2 -guanidinate interaction in **1** [2.024(2)–2.028(2) Å] and of the μ_2 -amidinate interaction in **2** [2.031(2)–2.045(2) Å]. The dihedral angle between the planes N1Fe1N2 and N4Fe1N8, and N5Fe2N7 and N10Fe2N11 in **1** are 94.7 and 90.3°, respectively, much larger than those of 87.3 and 85.3° formed by the planes N1Fe1N2 and N3Fe1N8, and N4Fe2N7 and N5Fe2N6 in **2**.

The N–Fe–N angles of the chelating guanidinate ligands in **1** are 63.86(9) and 64.07(9)°, comparable to those of the amidinate ligands in **2** [63.85(7) and 63.64(8)°]. Again, the comparable angles in **1** [133.53(10), 135.96(10)°] and **2** [137.95(8), 130.77(8)°] are associated with the $N\mu$ –Fe– $N\mu$ angles.

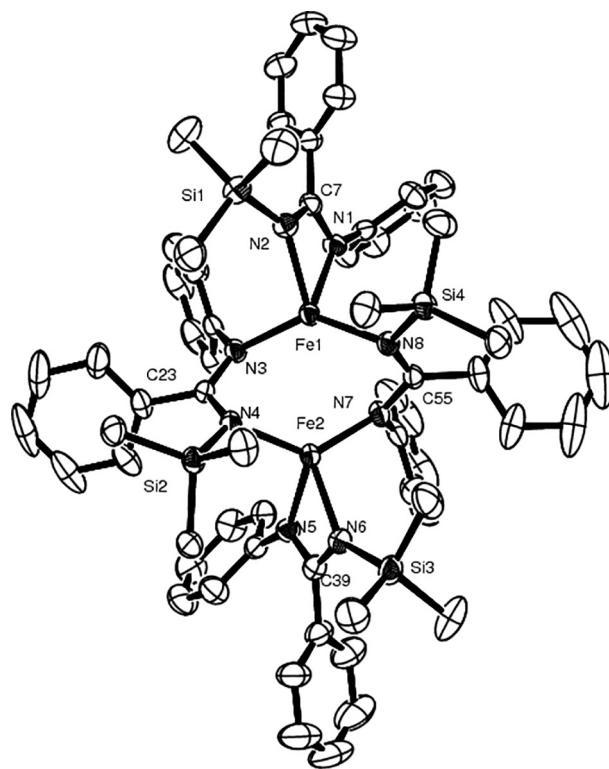


Fig. 2. Perspective ORTEP drawing of the molecular structure of **2**. All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 50% probability. Selected bond lengths (Å) and angles (deg): Fe(1)–N(1) 2.113(2), Fe(1)–N(2) 2.125(2), Fe(1)–N(3) 2.044(2), Fe(1)–N(8) 2.045(2), Fe(2)–N(5) 2.110(2), Fe(2)–N(6) 2.126(2), Fe(2)–N(4) 2.033(2), Fe(2)–N(7) 2.031(3), N(1)–C(7) 1.328(3), N(2)–C(7) 1.334(3), N(3)–C(23) 1.322(3), N(4)–C(23) 1.341(3), N(5)–C(39) 1.322(3), N(6)–C(39) 1.339(3), N(7)–C(55) 1.332(3), N(8)–C(55) 1.327(3); N(1)–Fe(1)–N(2) 63.85(7), N(3)–Fe(1)–N(8) 137.95(18), N(5)–Fe(2)–N(6) 63.64(8), N(4)–Fe(2)–N(7) 130.77(8), N(1)–C(7)–N(2) 114.7(2), N(3)–C(23)–N(4) 119.5(2), N(5)–C(39)–N(6) 114.1(2), N(7)–C(55)–N(8) 118.7(2).

A striking structural feature is the long Fe···Fe distance in **1** [3.383 Å] and in **2** [3.153 Å], which precludes the formation of any iron-iron bond. The distances fall in the range of other dinuclear compounds of the type $[\text{Fe}_2\text{X}_2]^{2+}$ (X = F or Cl), for which the metal atom separations are greater than 3.0 Å [24,25].

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