Inorganica Chimica Acta 394 (2013) 501–505

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Note

Synthesis, structure, and magnetic properties of the halide-bridged dimeric complex $[(bpmaL_1)Fe(\mu\text{-}Cl)Cl]_2$

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ARTICLE INFO

Article history:
Received 3 June 2012
Received in revised form 18 September 2012
Accepted 18 September 2012
Available online 29 September 2012

Keywords:
N,*N*-Bis{(1-H pyrazole-1-yl)methyl}aniline
Binuclear iron(II) complex
Magnetic susceptibility
α-Olefin polymerization

ABSTRACT

Complexation of $FeCl_2{\cdot}4H_2O$ with *N*,*N*-Bis{(1-H pyrazole-1-yl)methyl}aniline [$bpmaL_1$] gave air-stable dichloro-bridged binuclear iron(II) species (**1a**) having five-coordinated iron, which was characterised by X-ray crystallography and magnetic susceptibility. The geometry at each iron centre of **1a** is a distorted trigonal bipyramid with two equivalent half-molecules providing overall C_i symmetry. One of the pyrazolyl nitrogen atoms (N1) and a chlorine atom $(Cl2)^{\#}$ form one apex of the distorted trigonal bipyramid. The magnetic parameters indicated only a weak antiferromagnetic coupling, despite the presence of two chloro ions, and dominant zero-field-splitting parameters. The relatively long Fe···Fe distance of 3.8118(6) Å within the chloro-bridged dimer excludes direct interaction between the iron(II) ions. Thus, the antiferromagnetic coupling between the two iron(II) ions of **1a** is attributed to superexchange through the chloride ions. Compared to the analogous cobalt complexes, the activity of α-olefin polymerization towards ethylene, norbornene, 1-octene and methyl methacrylate (MMA) was virtually zero, **1a** is the first bis-pyrazole based dinuclear and five-coordinated iron(II) complex.

1. Introduction

Coordination complexes with pyrazole-based chelating ligands are of particular interest because of their many applications, e.g. as industrial catalysts for olefin oligomerisation and polymerisation [1–3], as bioinorganic materials in pharmaceutical preparations [4–8], and as catalytic materials [9,10]. As catalysts for olefin polymerisation, very little is known about bispyrazolyl ligand-based transition metal complexes [11–14] compared to especially those incorporating a tris-pyrazole ligand [15–20]. For example, the groups of Gibson and co-workers [21] and Brookhart and co-workers [22,23], independently discovered highly active tridentate iron and cobalt complexes having 2,6-bis(imino)pyridines as ligands. These were highly active for ethylene polymerisation. Similarly, the chelate pyrazolyl ligands were reported firstly by Driessen et al. [24], the transition metal complexes with bispyrazolyl ligands, specifically iron-bispyrazolyl complexes have been the best interested due to their spin state stability [25–30] and applications as various catalyst precursors [31–34]. Herein, we report the synthesis and characterisation of the iron(II) dimeric complexes, namely $[(bpmaL_n)Fe(\mu\text{-}Cl)Cl]_2$, where specifically ($bpmaL_1$) refers to *N*,*N*-bis(pyrazolylmethyl)aniline, having substituents on both the pyrazole ring and aniline ring units. The first goal of the research was to investigate the steric and electronic influences of the substituents on complex formation. Secondly, the catalytic behaviour of these modified methyl aluminoxane (MMAO)-activated complexes was additionally investigated for the polymerisation of α-olefins [35,36]. Surprisingly, they were catalytically inactive towards substrates containing the olefinic moiety, even towards methyl methacrylate (MMA). In contrast, the cobalt analogues $[bpmaL_n]CoCl_2$ [37], which was tetrahedral monomeric Co(II) complexes, towards MMA are very reactive towards MMA [36,38,39].

2. Experimental

2.1. Materials and instrumentation

All manipulations were performed using a combination of glove box, high vacuum, and Schlenk techniques under an argon atmosphere unless otherwise specified. Solvents were purified and degassed by standard procedures. Other starting materials were obtained from high-grade commercial suppliers and used without further purification. ^1H NMR (400 MHz, 600 MHz) and ^{13}C NMR (100.61 MHz, 150.85 MHz, respectively) were recorded on a Bruker Advance Digital 400, 600 NMR spectrometer and chemical shifts were recorded in ppm units using $SiMe_4$ as an internal standard. Coupling constants are reported in Hertz (Hz). Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha (neat) and the data are

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http://dx.doi.org/10.1016/j.ica.2012.09.010

reported in reciprocal centimetres. Melting point was measured by Digital Melting Apparatus (IA9100). Elemental analysis and ICP (Inductively Coupled Plasma) were performed by Fison-EA1108 and Thermo IRIS XDL duo, respectively. Magnetic susceptibilities were measured in an applied field of 5000 Oe between 6 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made [545.5 (**1**), 426.5 (**2**) and 534.8 × 10^{-6} (**3**) emu/mol] by using Pascal's constants.

2.2. Synthesis of ligands and complexes

2.2.1. Preparation of ligands

(1-H Pyrazole-1-yl)methanol as starting material were prepared in processes described elsewhere [21,32]. Ligands *N*,*N*-Bis{(1-H-Pyrazole-1-yl)methyl}aniline, [bpmaL$_1$], *N*,*N*-Bis{(1-H-Pyrazole-1-yl)methyl}-2,4,6-trimethylaniline, [bpmaL$_2$], *N*,*N*-Bis{(1-H Pyrazole-1-yl)methyl}2,6-diisopropylaniline, [bpmaL$_3$], *N*,*N*-Bis{(3,5-dimethyl-1H-pyrazol-1-yl)methyl}-2,6-diisopropylaniline, [bpmaL4] was prepared by by a similar procedure as described in the literature [36–39].

2.2.2. Synthesis of [(bpmaL$_1$)Fe(μ-Cl)Cl]$_2$ (**1a**)

The solution of ligand [bpmaL$_1$] (1.00 g, 3.95 mmol) in dried ethanol (50 mL) was added to the solution of $FeCl_2{\cdot}4H_2O$ (0.780 g, 3.95 mmol) in dried ethanol (50 mL) at room temperature. The pale yellow solid was precipitated after stirring at room temperature for 24 h. The solid was filtered and washed with fresh cold ethanol (30 mL × 3) followed by washing with pentane (30 mL × 3) to give pale yellow coloured crystalline solid (2.33 g, 77.5%). m.p = 138–139 °C. *Anal.* Calc. for $C_{28}H_{30}Cl_4Fe_2N_{10}$: C, 44.24; H, 3.98; N, 18.43. Found: C, 44.26; H, 3.98; N, 18.62%. ^{1}H NMR (DMSO, 400 MHz): δ 7.77 ($[-(N_2C_3\mathit{H}_3)_2-]$, s, 2H, $J = 0.15$ Hz), 7.43 ($[-(N_2C_3\mathit{H}_3)_2-]$, d, 2H, $J = 0.15$ Hz), 7.06 ($[C_6\mathit{H}_5(CH_3)_3N-]$, s, 2H), 6.74 ($[C_6\mathit{H}_5(CH_3)_3N-]$, d, 3H), 6.23 ($[-(N_2C_3\mathit{H}_3)_2-]$, d, 2H, $J = 0.38$ Hz), 5.42 ($[-N(C\mathit{H}_2)_2-]$, s, 2H), 5.34 ($[-N(C\mathit{H}_2)_2-]$, s, 2H). IR (solid neat; cm^{-1}): 1496 (w), 11468 (m), 1453 (w), 1400 (m), 1375 (w), 1335 (w), 1312 (w), 1289 (w), 1247 (w), 1218 (w), 1183 (m), 1145 (m), 1106 (w), 1098 (w), 1070 (m), 1045 (m), 977 (m), 931 (m), 892 (w), 871 (w), 849 (w), 829 (w), 808 (w), 779 (s), 766 (s), 721 (m), 697 (s), 678 (m), 656 (m), 639 (m), 619 (m), 610 (s), 590 (m), 579 (m), 570 (m).

2.2.3. Synthesis of [(bpmaL$_2$)Fe(μ-Cl)Cl]$_2$ (**2a**)

The solution of ligand [bpmaL$_2$] (1.00 g, 3.39 mmol) in dried ethanol (50 mL) was added to the solution of $FeCl_2{\cdot}4H_2O$ (0.673 g, 3.39 mmol) in dried ethanol (50 mL) at room temperature. The pale yellow solid was precipitated after stirring at room temperature for 48 h. The solid was filtered and washed with fresh cold ethanol (30 mL × 3) followed by washing with pentane (30 mL × 3) to give pale yellow coloured crystalline solid (0.75 g, 51.8%). m.p = 173–174 °C. *Anal.* Calc. for $C_{34}H_{42}Cl_4Fe_2N_{10}$: C, 48.37; H, 5.01; N, 16.59. Found: C, 48.08; H, 5.03; N, 16.43. ^{1}H NMR (DMSO, 400 MHz): δ 7.96 ($[-(N_2C_3\mathit{H}_3)_2-]$, s, 2H, $J = 0.15$ Hz), 7.42 ($[-(N_2C_3\mathit{H}_3)_2-]$, d, 2H, $J = 0.15$ Hz), 6.66 ($[C_6\mathit{H}_2(CH_3)_3N-]$, s, 2H), 6.46 ($[-(N_2C_3\mathit{H}_3)_2-]$, s, 2H, $J = 0.38$ Hz), 5.13 ($[-N(C\mathit{H}_2)_2-]$, s, 4H), 2.05 ($[C_6H_2(C\mathit{H}_3)_3N-]$, d, 3H), 1.95 ($[C_6H_2(C\mathit{H}_3)_3N-]$, d, 3H), 1.50 ($[C_6H_2(C\mathit{H}_3)_3N-]$, s, 3H). IR (solid neat; cm^{-1}): 2922 (m), 2853 (w)1514 (w), 1482 (w), 1468 (w), 1451 (w), 1403 (m), 1352 (w), 1320 (w),1302 (m), 1250 (m), 1205 (w), 1189 (m), 1168 (m), 1157 (m), 1126 (m), 1098 (m), 1061 (m), 989 (w), 974 (m), 941 (m), 908 (w), 892 (w), 861 (w), 846 (m), 807 (w), 763 (s), 733 (m), 677 (m), 645 (m), 608 (m), 589 (s), 559 (w).

2.2.4. Synthesis of [(bpmaL$_3$)Fe(μ-Cl)Cl]$_2$ (**3a**)

The solution of ligand [bpmaL$_3$] (1.00 g, 2.54 mmol) in dried ethanol (50 mL) was added to the solution of $FeCl_2{\cdot}4H_2O$ (0.510 g, 2.54 mmol) in dried ethanol (50 mL) at room temperature. The pale yellow solid was precipitated after stirring at room temperature for 24 h. The solid was filtered and washed with fresh cold ethanol (30 mL × 1) followed by washing with pentane (30 mL × 2) to give pale yellow coloured crystalline solid. Yield (0.94 g, 79.6%). m.p = 182–183 °C. *Anal.* Calc. for $C_{40}H_{54}Cl_4Fe_2N_{10}$: C, 51.75; H, 5.86; N, 15.09. Found: C, 52.13; H, 6.19; N, 14.45%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 ($[-(N_2C_3\mathit{H}_3)_2-]$, s, 2H), 7.49 ($[-(N_2C_3\mathit{H}_3)_2-]$, s, 2H), 7.18 ($[C_6\mathit{H}_3(CH)_2\ (CH_3)_4N-]$, s, 3H), 6.27 ($[-(N_2C_3\mathit{H}_3)_2-]$, s, 2H), 5.50 ($[-N(C\mathit{H})_2-]$, s, 4H), 2.65 ($[C_6H_3(C\mathit{H})_2(CH_3)_4N-]$, s, 2H), 0.90($[C_6\mathit{H}_3(CH)_2(C\mathit{H}_3)_4N-]$, s, 6H), 1.05 ($[C_6H_2(C\mathit{H}_3)_4N-]$, s, 6H). IR (solid neat; cm^{-1}): 2922 (m), 2854 (m), 1739(w), 1709 (w), 1467 (m), 1454 (m), 1441 (m), 1405 (s), 1362 (m), 1322 (m), 1297 (m), 1252 (m), 1204 (m), 1170 (s), 1113 (m), 1099 (m), 1068 (s), 1053 (m), 989 (m), 973 (m), 948 (m), 917 (m), 899 (m), 866 (w), 812 (m), 781 (s), 769(s), 748 (s), 657 (w), 643 (m), 608 (s), 588 (s).

2.3. Representative polymerization procedure of MMA

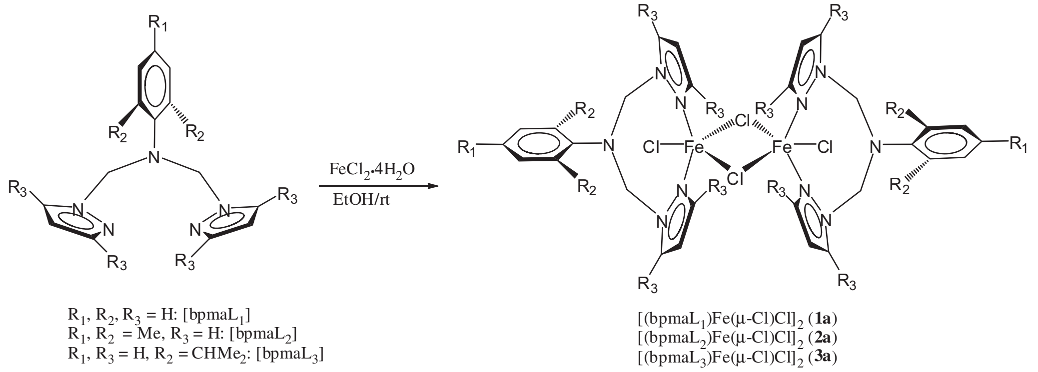
Methyl methacrylate (MMA) was extracted with 10% sodium hydroxide, washed with water, dried over magnesium sulfate, and distilled over calcium hydride under reduced pressure before use. To a 100-mL Schlenk flask containing [bpmaL]$CoCl_2$ (11.4 mg, 15.0 μmol) in toluene (1 mL) was added MMAO (modified methylaluminoxane, 6.9 wt.% in toluene, 3.25 mL, $[MMAO]_0/[Fe(II)\ catalyst]_0 = 500$) under a dry argon atmosphere. After the mixture had been stirred at room temperature for 10 min, it was transferred into MMA (5.0 mL, 47.0 mmol, $[MMA]_0/[F(II)\ catalyst]_0 = 3100$). Then, the reaction flask was immersed in an oil bath at 60 °C and stirred for 2 h. The resulting polymer was precipitated in methanol (400 mL) and HCl (3 mL) was added with stirring for 10 min. The polymer was filtered and washed with methanol (400 mL × 3) to give PMMA, which was vacuum-dried at 60 °C. Additionally, polymerization was examined at different temperatures (0, 25, 40, 50 °C) with **1a**.

2.4. X-ray crystallographic analysis

An X-ray quality single crystal was mounted in a thin-walled glass capillary on an Enraf-Noius CAD-4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10° < \theta < 13°$). Intensity data were collected with θ range of 1.83–25.46° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 h during data collection. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with χ-scans were applied to the data. The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on *F* using SHELX-97 and SHELX-97 program packages. All non-hydrogen atoms were refined positioned geometrically using riding model with fixed isotropic thermal factors. The final cycle of the refinement converged with $R_1 = 0.0363$ and $wR_2 = 0.0864$.

3. Results and discussion

The [(bpmaL$_n$)Fe(μ-Cl)Cl]$_2$ complexes were readily prepared by stirring a solution of $FeCl_2{\cdot}4H_2O$ with one equivalent of the (bpmaL$_n$) ligand [40] in dry ethanol at room temperature (Scheme 1). The complexes were isolated in high yield as air-stable microcrystalline yellow powders. However, the dimeric iron complex [(bpmaL$_4$)Fe(μ-Cl)Cl]$_2$ (**4a**) did not form with ligand ([bpmaL$_4$],



R_1, R_2, R_3 = H: [bpmaL$_1$]
R_1, R_2 = Me, R_3 = H: [bpmaL$_2$]
R_1, R_3 = H, R_2 = CHMe$_2$: [bpmaL$_3$]

[(bpmaL$_1$)Fe(μ-Cl)Cl]$_2$ (**1a**)
[(bpmaL$_2$)Fe(μ-Cl)Cl]$_2$ (**2a**)
[(bpmaL$_3$)Fe(μ-Cl)Cl]$_2$ (**3a**)

Scheme 1. Synthetic scheme for the preparation of [(bpmaL$_n$)FeCl-(μ-Cl)]$_2$ (**1a**–**3a**).

R_1 = H, R_2 = CHMe$_2$, R_3 = Me), presumably because of steric hindrance by the pyrazole substituent.

Dinuclear Fe complexes **1a**–**3a** were very inert to ethylene, 1-octene and norbornene polymerization, for example, for ethylene polymerization even at an ethylene pressure of 30 bar in toluene media at various temperatures. This catalytic inactivity of Fe(II) complex as a dimeric five-coordinated was totally different compared to bis(imino)pyridine–Fe(II) complex which shows high catalytic activity for ethylene polymerization and α-olefin oligomerization. However, only precatalyst **1a** could be activated with MMAO to polymerize methyl methacrylate (MMA) to give PMMA with T_g 120 °C. To confirm the catalytic activity of MMA polymerization, blank polymerization of MMA was performed with starting Fe complex, $FeCl_2{\cdot}4H_2O$, and MMAO themselves at 60 °C. The activity of **1a** was 0.34×10^6 g/mol Fe h, while those of $FeCl_2{\cdot}4H_2O$ and MMAO were only 0.21×10^5 g/mol Fe h and 0.14×10^5 g/mol Fe h at 60 °C, respectively.

A single crystal of [(bpmaL$_1$)Fe(μ-Cl)Cl]$_2$ (**1a**) was grown by slowly evaporating a methylene chloride solution at room temperature. The X-ray structure determination revealed a chloro-bridged dimeric species with crystallographic inversion symmetry (Fig. 1). Crystal structure data, details of data collection, and refinement parameters for **1a** are listed in Table 1. Selected bond lengths (Å) and angles (°) for **1a** are described in Fig. 1. The geometry at each iron centre is best described as a distorted trigonal bipyramid (TBP) with two equivalent half-molecules providing overall C_i symmetry. One of the pyrazolyl nitrogen atoms (N1) and a chlorine atom (Cl2)$^{\#}$ form one apex of the distorted trigonal bipyramid. There is

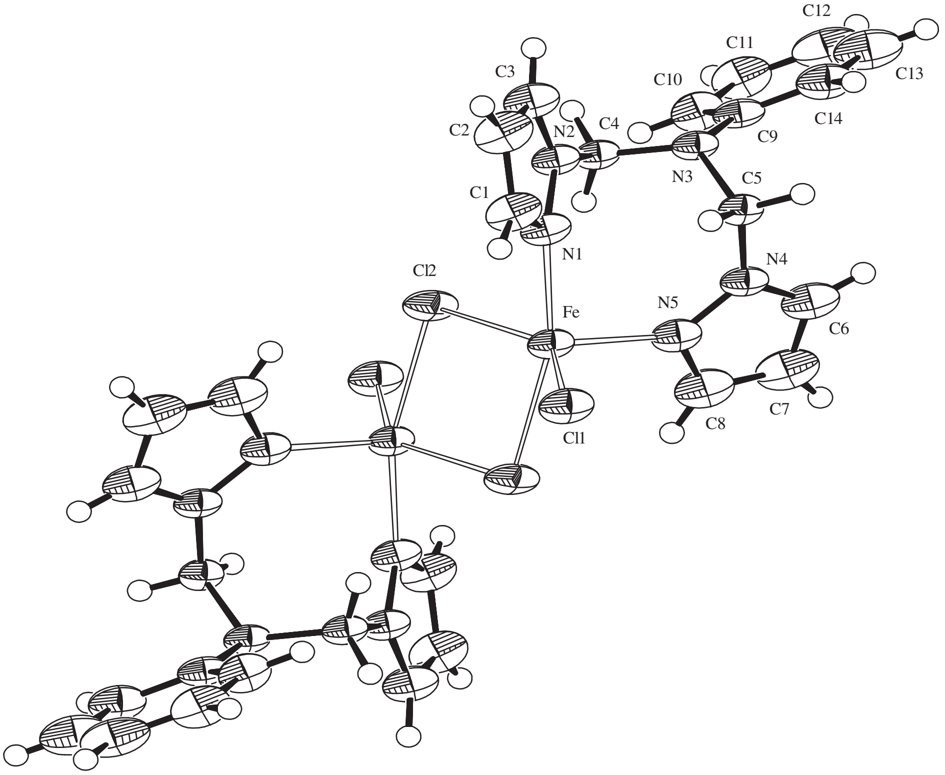


Fig. 1. ORTEP drawing and atom numbering of [(bpmaL$_1$)Fe(μ-Cl)Cl]$_2$ (**1a**) with 40% of the thermal ellipsoid probability. Selected bond lengths (Å) and angles (°) are Fe–Cl(1) 2.2827 (6), N(1)–N(2) 1.355(2), Fe–Cl(2) 2.3545 (6), N(2)–C(4) 1.451(3), Fe–Cl(2)$^{\#}$ 2.6367 (6), N(3)–C(9) 1.430(3), Cl(2)–Fe$^{\#}$ 2.6367 (9), N(3)–C(5) 1.451(2), Fe–N(1) 2.1791 (17), N(4)–C(5) 1.466(3), Fe–N(5) 2.1345 (17), Fe–Fe$^{\#}$ 3.8118 (6), Fe–Cl(2)–Fe$^{\#}$ 99.431 (19); N(1)–N(2)–C(4) 120.78(16), Cl(1)–Fe–Cl(2) 136.63 (3), C(5)–N(3)–C(4) 114.47(15), Cl(2)–Fe–Cl(2)$^{\#}$1 80.569 (19), N(5)–N(4)–C(5) 123.56(16), N(1)–Fe–Cl(1) 93.18 (5), N(4)–N(5)–Fe 132.46(13), N(5)–Fe–Cl(1) 112.05 (5), N(3)–C(5)–N(4) 114.61(16), N(1)–Fe–Cl(2)$^{\#}$1 165.34 (5), C(9)–N(3)–C(5) 116.28(16), N(5)–Fe–Cl(2)$^{\#}$1 92.59 (5), C(9)–N(3)–C(4) 115.32(16).

Table 1
Crystal data and structure refinement of [(bpmaL$_1$)Fe(μ-Cl)Cl]$_2$ (**1a**).

Empirical formula	$C_{28}H_{30}Cl_4Fe_2N_{10}$
Formula weight	760.12
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.9804(5)
b (Å)	9.8764(5)
c (Å)	10.5081(8)
V (Å^3)	819.41(10)
Z	1
D_{calc}	1.540 Mg/m^3
Absorption coefficient	1.248 mm^{-1}
$F(000)$	388
$F(000')$	389.35
Crystal size (mm)	0.50 × 0.40 × 0.30
θ (°)	2.20–25.47
Index ranges	$-10 \leq h \leq 10$ $0 \leq k \leq 11$ $-12 \leq l \leq 11$
Reflections collected/unique	3037 unique [R_{int} = 0.0097]
Reflections observed (>2σ)	3304
Data completeness	1.000
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3037/0/199
T_{min}, T_{max}	0.555, 0.688
$T_{min'}$	0.530
Goodness-of-fit (GOF) on F^2	1.114
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0296, wR_2 = 0.0838
R indices (all data)	R_1 = 0.0363, wR_2 = 0.0864
Largest difference in peak and hole (e Å^{-3})	0.595 and −0.358

a substantial enlargement of the Cl1–Fe–Cl2 angle [136.63(3)°] and a small contraction of the N5–Fe–Cl1 angle [112.05(5)°] in the equatorial plane. The N1–Fe–Cl(2*) angle is slightly less than 180° [165.34(5)°], and the N1–Fe–N5 angle is substantially larger [100.35(7)°] as a consequence of the bulky eight-membered chelate ring. The angles between the three equatorial ligands, Cl1–Fe–Cl2 [136.63(3)°], N5–Fe–Cl1 [112.05(5)°], and N5–Fe–Cl2 [110.22(5)°] total 358.86°. The Fe–N bond lengths are unexceptional, whereas the terminal Fe–Cl bond [2.2827(6) Å] is shorter than the bridging bond [2.3545(6) Å]. The chlorine atom bridges are notably asymmetric with bond lengths of 2.3545(6) Å for Fe–Cl2 and 2.6367(6) Å for Fe–Cl2$^{\#}$. Dinuclear, five-coordinate iron complexes with bridging units such as oxygen and halide are abundant [41–51]. However, trigonal bipyramidal diiron complexes, especially those containing the bis-pyrazole chelate ligand and bridged μ^2-chloro group, are uncommon [48]. The molecular structure of **1a** is similar to those of dichloro-(2-pyridylmethylidene)(triphenylsilyl)amino iron(II) [52], [2-(iminoethyl)pyridine]iron(II) [53], and bis(μ^2-chloro)-chloro-(2-(2′-pyridyl)quinoxaline)iron(II). In dichloro-(2-pyridylmethylidene)(triphenylsilyl)amino iron(II), which has a trigonal bipyramidal environment about iron, the N2 and Cl1A atoms are arranged in axial positions (N2–Fe–Cl1A, 170.98(6)°) while the N1, Cl1, and Cl2 atoms form the trigonal plane. The angles between the equatorial ligands are [N2–Fe1–N1] 81.86(9)°, [N2A–Fe1–N1] 122.30(9)°, [N2–Fe1–N2A] 143.4(1)°, and [N1–Fe–N1A] 102.7(1)°. For the [2-(iminoethyl)pyridine] iron(II) complex, the pyridyl nitrogen atom N1 and Cl1 mark one apex of the distorted trigonal bipyramid, with N1–Fe–Cl1 = 155.6(2)°. The angles between the three equatorial ligands are [N9–Fe–Cl1*] 126.0(2)°, [N9–Fe–Cl2] 116.7(2)°, and [Cl1*–Fe–Cl2] 115.5(1)°. These angles define a distorted trigonal bipyramid having an enlarged Cl–Fe–Cl angle [133.9(1)°] and asymmetric chlorine bridges having lengths 2.511(1) Å [Fe–Cl2] and 2.391(1) Å [Fe–Cl2*].

The magnetic susceptibility (χ) of **1a** was measured from 6 to 350 K at 1 T field strength to study the effect of the structural parameters on the magnetic properties (Fig. 2). An MPMS XL 7.0 magnetometer was used for the measurements. The effective magnetic moment, μ_{eff} [=$(8\chi_M T)^{1/2}$] was 7.43 μ_B/Fe$_2$ at 350 K. This value is slightly larger than the 6.93 μ_B expected for two independent iron(II) ions ($S = 2$, Fe(II), $g = 2$). The value of $\mu_{eff}(T)$ decreased with decreasing temperature, consistent with the presence of a weak antiferromagnetic interaction between the iron(II) ions. The $\mu_{eff}(T)$ data were fitted to an analytical expression for $\chi(T)$ for a coupled $S = 2$ binuclear spin model based on the Hamiltonian $H = -2JS_1{\cdot}S_2 + 2D_{Fe}[S_z{}^2 - 2] + g\mu_B(S_1 + S_2){\cdot}B$ ($S_1 = S_2 = 2$) incorporating exchange coupling, zero-field splitting (D), and Zeeman interaction [54]. The fitting gave $J = -0.86$ cm^{-1} with $g = 2.15$, $|D| = 1.332$ cm^{-1}, and 0.9% paramagnetic impurities. The resulting magnetic parameters indicated only a weak antiferromagnetic coupling, despite the presence of chloro ions, and dominant zero-field-splitting parameters [55]. The coupling constant J of **1a** is quite different than the −63.7 cm^{-1} value for [(PhCN)$_2$(Mes)$_2$Fe$_2${μ-N = C(Mes)(Ph)}$_2$] (Mes = 2,4,6-Me$_3$C$_6$H$_2$), which is also a nitrogen-bridged dinuclear iron(II) system [56]. The relatively long Fe⋯Fe distance (3.8118(6) Å) within the chloro-bridged dimer rules out direct interaction between the iron(II) ions. Therefore, the antiferromagnetic coupling between the two iron(II) ions of **1a** is attributed to superexchange through the chloride ions.

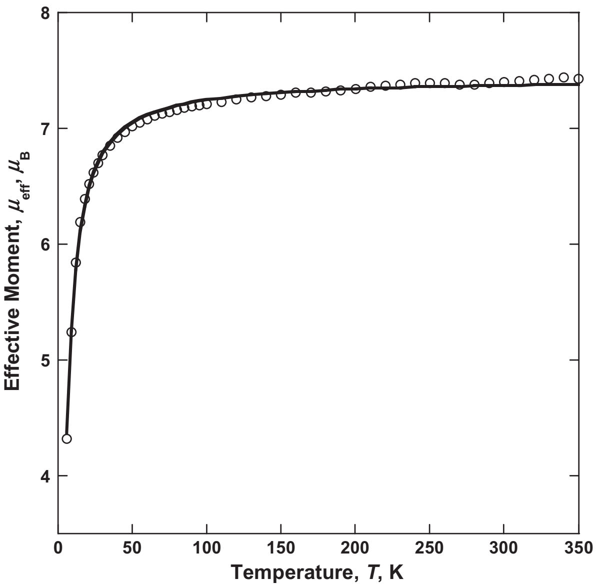


Fig. 2. Plot of $\mu_{eff}(T)$ for [(bpmaL$_1$)Fe(μ-Cl)Cl]$_2$ (**1a**) in a field of 1 T. Solid line shows the best fit obtained.

4. Conclusion

The first bispyrazole-containing binuclear and five-coordinated iron(II) complex [(bpmaL$_1$)Fe(μ-Cl)Cl]$_2$ (**1a**) have been structurally characterised. In addition, the magnetic properties have been measured for the iron(II) bimetallic **1a**. The magnetic property of dimeric iron complex is best described as only a weak antiferromagnetic coupling between the two iron(II) ions of **1a** and dominant zero-field-splitting parameters.

Acknowledgments

This research was supported under the Basic Science Research Programs through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science, and Technology (Grant No. 2009-0075742). This research was supported by Research fund of Kyungpook National University, 2012.

Appendix A. Supplementary material

The supplementary crystallographic data for **1a** can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.09.010.

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