The Syntheses of (Chloro) Iron(II) Complexes by Using Tridentate Polypyridine Ligands

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Two (chloro)iron(II) complexes have been synthesized and characterized by crystallography.

Many inorganic complexes possessing polypyridine ligands have been reported as structural models or functional models for non-heme iron monooxygenases[1] or dioxygenases.[2] Many of the works have been done by use of tetradentate ligand, tpa (tris(2-pyridylmethyl)amine), while the availability of tridentate ligand, bpa (bis(pyridylmethyl)amine) was not investigated extensively in this field.

Here we report the structures of two (chloro)iron(II) complexes by use of bpea[3] and blea[4] (bpea = bis(2-pyridylmethy)ethylamine, blea = bis(6-methyl-2-pyridylmethyl) ethylamine).

A mixture of 1.00 g (7.89 mmol) of $FeCl_2$ and 1.79 g (7.89 mmol) of bpea was stirred under argon in 10 ml of MeOH overnight. The pale brown solid of $FeCl_2$ disappeared. Instead, precipitation of a yellow-orange solid was observed. The solid was filtered and recrystallized in ethanol to give prismatic crystals of $(\mu\text{-Cl})_2$diiron(II) complex, (bpea)Fe(II)(Cl)$(\mu\text{-Cl})_2$Fe(II)(Cl)(bpea) (**1**) (1.20 g, yield 43%).[6] The structure of **1** is shown in Figure 1.[7] The crystal system indicates the center of imposed symmetry. Each metal in complex **1** shows slightly distorted octahedral with N3Cl3 donor set. The ligand, bpea, in **1** shows facial coordination mode. The two bond distances of Fe-μ-Cl (2.4982(8) Å, 2.5328(7) Å) differ in length, due to difference in the trans ligands. They are longer than those of other reported $(\mu\text{-Cl})_2$diiron(II) complexes, ; 2.396(2) Å for $[(tpa)Fe(II)(\mu\text{-Cl})_2Fe(II)(tpa)]\ (ClO_4)_2$[8] and 2.370(2) Å for $[(tmpza)Fe(II)(\mu\text{-Cl})_2Fe(II)(tmpza)](ClO_4)_2$[8] (tmpza = tris(3,5-dimethyl-1-pyrazlylmethyl)amine). The bond distance of terminal Fe-Cl (2.3657(7) Å) is expectedly shorter than the Fe-μ-Cl bond in **1**, while it is longer than those found in other known (chloro)iron(II) complexes; 2.25(1) Å for $[Fe_2Cl_2(OC_6H_4\text{-p-}Me)_2]^{2-}$,[9] 2.29(1) Å for $FeCl_4^{2-}$,[10] 2.23(1) Å for $Fe(Cl)[BH(3\text{-}Bu^tpz]_3)$[11] and 2.204(2) Å for $Fe(Cl)[BH(3,5\text{-}Pr^i{}_2pz)_3]$ ($[BH(3\text{-}Bu^tpz)_3]^-$ = hydrotris(3-t-butyl-1-pyrazolyl)borate, $[BH(3,5\text{-}Pr^i{}_2pz)_3]^-$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate).[12] The $Fe\text{-}N_{amine}$ distance (2.333(2) Å) is longer than $Fe\text{-}N_{pyridine}$ (2.192(2), 2.213(2) Å), which must be due to the steric requirement of the chelate bpea ligand. The N_{amine} atom in **1** appears to be unable to locate at its right position for the ideal coordination toward the central atom.

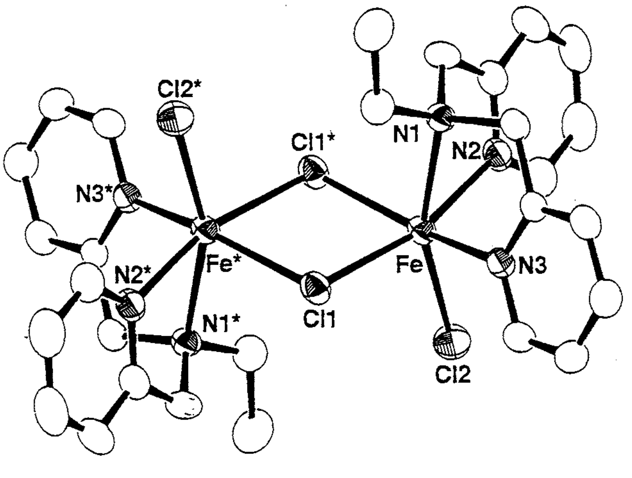

Figure 1. ORTEP view of Complex **1**. Selected distances (Å) and angles (deg): Fe-Cl1 2.4982(8); Fe-Cl1* 2.5328(7); Fe-Cl2 2.3657(7); Fe-N1 2.333(2); Fe-N2 2.192(2); Fe-N3 2.213(2); Cl1-Fe-Cl1* 82.95(2); Cl1-Fe-Cl2 97.20(2); Cl1-Fe-N1 99.29(5); Cl1-Fe-N2 89.17(5); Cl1-Fe-N3 166.16(5); Cl1*-Fe-Cl2 102.05(3); Cl1*-Fe-N1 93.33(5); Cl1*-Fe-N2 164.29(5); Cl1*-Fe-N3 86.26(5); Cl2-Fe-N1 158.68(5); Cl2-Fe-N2 92.38(5); Cl2-Fe-N(3) 93.52(6); N1-Fe-N2 74.50(7); N1-Fe-N3 72.64(7); N2-Fe-N3 99.15(7); Fe-Cl1-Fe1* 97.05(2).

The reaction of $FeCl_2$ with blea (bis(6-methyl-2-pyridylmethyl)ethylamine) was performed to elucidate how the methyl substitutents in this ligand system effect the geometry of the complex. Treatment of $FeCl_2$ (1.00 g, 7.89 mmol) with blea (2.23 g, 7.89 mmol) in ethanol gave monomeric (chloro)iron(II) complex, $FeCl_2$(blea) (**2**). Recrystallization in ethanol gave yellow cubic crystal (2.00 g yield 62%).[13] The structure of **2** is shown in Figure 2.[14,15] The structure shows monomeric

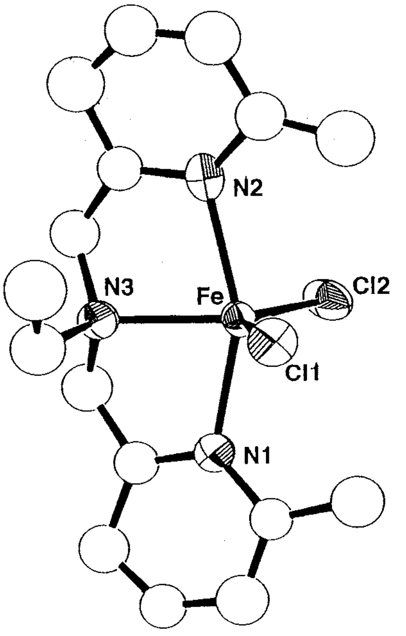

Figure 2. ORTEP view of Complex **2**. Selected distances (Å) and angles (deg): Fe-Cl1 2.299(6); Fe-Cl2 2.321(5); Fe-N1 2.23(1); Fe-N2 2.29(1); Fe-N3 2.18(1); Cl1-Fe-Cl2 131.6(2); Cl1-Fe-N1 96.0(4); Cl1-Fe-N2 96.4(4); Cl1-Fe-N3 114.2(4); Cl2-Fe-N1 92.1(3); Cl2-Fe-N2 94.6(3); Cl2-Fe-N3 114.2(4); N1-Fe-N2 156.3(5); N1-Fe-N3 77.4(5); N2-Fe-N3 79.1(5).

pseudo trigonal bipyramidal with N3Cl2 donor set. The geometry of blea in complex **2** is meridional, not facial. As N1 and N2 can be regarded as axial ligands in this complex, the angle of N1-Fe-N2 (156.3°) suggests that distorted trigonal bipyramidal structure of **2**, owing to the steric requirement of blea. The Fe-Cl bond distances (2.299(6) Å, 2.321(5) Å) in **2** are shorter than the terminal Fe-Cl bond length in **1** but, longer than the value in previously reported complexes (*vide supra*). It is notable that methyl substitutent at 6-position of pyridine ring in tridentate polypyridine ligand causes such geometrical change from six coordination of **1** to five coordination of **2**. This structural difference can be ascribed to the presence of 6-methyl groups which sterically prevent the two pyridines from approaching closely to the metal center. We believe that both complexes can serve as good starting materials for the model complexes of non-heme iron proteins.

References

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3 The ligand, bpea was synthesized by previously reported method. See; S. Pal, M. K. Chan, and W. H. Armstrong, *J. Am.Chem. Soc.*, **114**, 6398(1992).

4 The ligand, blea was synthesized by reacting 2-chloromethyl-6-methyl-pyridine with ethylamine in aqueous alkaline solution.

6 Analytically pure solid of **1** was obtained by the recrystallization in EtOH (yield ca. 43%). Anal. Found: C, 47.03; H, 4.83; N, 12.01%. Calcd for **1** C_{28} Cl_4 Fe_2 H_{34} N_6: C. 47.51; H. 4.80; N. 11.86%. IR(KBr, cm^{-1}), ν(C=C), 1603.

7 The structure was solved by direct methods (MITHRIL) and refined by the full matrix least squares techniques with TEXSAN. All non-hydrogen atoms were refined isotropically, and they were refined anisotropically. Hydrogen atoms were calculated and fixed in final refinement cycles. Complex 1 was crystallized in monoclinic space group *P1 21/a 1* (no.14) with a = 10.016(2) Å, b = 16.174(3) Å, c = 10.098(2) Å, α = 110.19(1)°, V = 1535.4(5) Å^3, and Z = 2. The *R(Rw)* value is 0.0345(0.0337) for 3559 reflections 3° < θ < 60°, $Fo > 2\sigma(Fo)$.

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13 Analytically pure solid of **2** was obtained by the recrystallization in EtOH (yield 62%). Anal. Found: C, 50.76; H, 5.23; N, 11.34%. Calcd for **2** C_{16} Cl_2 Fe_1 H_{21} N_3: C. 50.32; H. 5.50; N. 11.00%. IR(KBr, cm^{-1}), ν(C=C), 1603.

14 The structure was solved by direct methods (MITHRIL) and refined by the full matrix least squares techniques with TEXSAN. All non-hydrogen atoms were refined isotropically, and iron atom and ligated nitrogen and chlorine atoms were refined anisotropically. Hydrogen atoms were calculated and fixed in final refinement cycles. Complex 1 was crystalized in monoclinic spcace group *P1 21/n* (No. 14) with a = 8.653(4) Å, b = 12.010(6) Å, c = 17.256(3) Å, β = 96.18(3)°, V = 1783(1) Å^3, and Z = 4. The *R(Rw)* value is 0.1028(0.0925) for 1206 reflections 3.4° < 2θ < 55°, $Fo > 2\sigma(Fo)$.

15 A five coordinate bis(chloro)iron(II) complex which shows similar geometrical feature of **2** has attracted considerable attention as highly active catalysts to polymerize olefins. See; B. L. Small, M. Brookhart, and M. A. Bennett, *J. Am. Chem. Soc.*, **120**, 4049(1998).