Synthesis of an iron(ii) complex versatile for preparation of iron(ii) complexes with novel pentadentate ligands *via* C–C bond formation with various nitriles: 1,3-dimethyl-1,3-propanediylidenebis(2-pyridylmethanamine)iron(ii) perchlorate

Masafumi Goto,*[a] Yoshinobu Ishikawa,[a] Takao Ishihara,[a] Chika Nakatake,[a] Tomoe Higuchi,[a] Hiromasa Kurosaki[a] and the late Virgil L. Goedken[b]

[a] *Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862, Japan*
[b] *Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3006, USA*

A bis(acetonitrile)iron(II) complexes with 1,3-dimethyl-1,3-propanediylidenebis(2-pyridylmethanamine) undergoes a nucleophilic addition to the nitrile carbon on addition of triethylamine to a nitrile solution yielding mono(acetonitrile)iron(II) complex with a novel pentadentate polyimine ligand.

A tetradentate ligand containing a 1,3-diimine moiety, 1,3-dimethyl-1,3-propanediylidenebis(2-pyridylmethanamine), L, which is formally derived from acetylacetone and 2-(aminomethyl)pyridine, is expected to coordinate to metal ions leaving two coordination sites for other ligands. In this report, we describe the synthesis of the iron(ii) complex with this ligand and its reaction products with acetonitrile and [$^2H_3$]acetonitrile and their structures obtained by X-ray crystallography.

The iron(ii) complex, *trans*-[FeL(MeCN)$_2$][ClO$_4$]$_2$·MeCN **1** was prepared in moderate yield (50–60%) under strict anaerobic and dehydrated conditions by successive additions of precursor tridentate ligand MeCOCH$_2$C(Me)=NHCH$_2$C$_5$H$_4$N and 2-(aminomethyl)pyridine to an acetonitrile solution of [Fe(MeCN)$_6$]$^{2+}$ prepared *in situ*.[†] These crystals were not stable under air and even stored in a vacuum were potentially explosive.

The structure of **1** was determined by X-ray crystallography and that of the cation is shown in Fig. 1.[‡] Two acetonitriles coordinate *trans* to each other to form a distorted octahedral geometry. The six-membered chelate ring of the 1,3-diimine moiety is almost planar with a mean deviation of 0.042 Å and a largest deviation of 0.076(6) Å at C(8). The two pyridine rings swing away from each other in order to evade the intramolecular repulsion between two 6-position hydrogen atoms on each pyridine to give a dihedral angle of 30.95° between two pyridine rings as found for *trans*-bis(bipyridine)palladium complexes.[1]

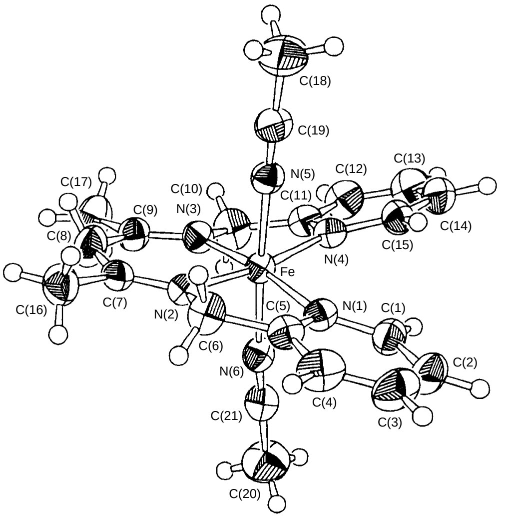

Fig. 1 Molecular structure of the cation of **1** showing the atom numbering scheme

This complex showed a C≡N stretching band at 2244 cm^{-1} and weak absorption band at 527 nm (ε = 150 dm^3 mol^{-1} cm^{-1}) for an acetonitrile solution. The variable-temperature ^{1}H NMR spectra of this compound[§] exhibited seven signals which obey non-Curie dependency similar to that reported about intersystem crossing polypyridyl ferrous complexes.[2]

The C–C bond formation between a coordinated tetradentate ligand and a (coordinated) acetonitrile occurred at room temperature within 2 h on addition of a small amount of triethylamine to an acetonitrile solution of **1**. Orange crystals of the iron(ii) complex of 2-(1-iminoethyl)-1,3-dimethyl-1,3-propanediylidenebis(2-pyridylmethanamine), L′, [FeL′(MeCN)][ClO$_4$]$_2$·thf, **2** were used for crystal structure determination. These are two crystallographically independent molecular ions with almost identical structures and two thf molecules in the asymmetric unit: one of the molecular ions is shown in Fig. 2.[‡] The tetradentate moiety adopts *cis*-β coordination and the

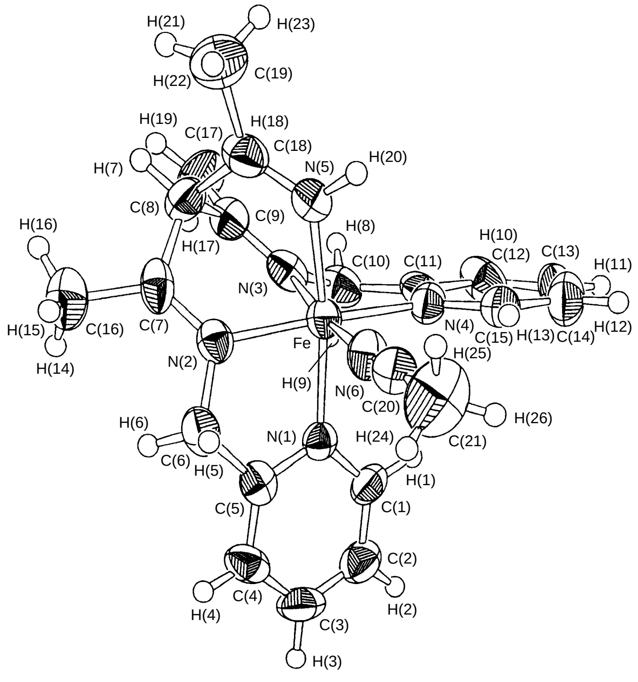

Fig. 2 Molecular structure of one of the crystallographically independent cations of **2** showing the atom numbering scheme

acetonitrile was fused to the central carbon atoms of the 1,3-diimine moiety. One trigonal face is occupied by the three isolated imines which are linked to the tetrahedral C(8) and the C=N bond distances are N(2)–C(7) 1.31(1), N(3)–C(9) 1.28(1) and N(5)–C(18) 1.29(1) Å. The six-membered chelate rings of FeN(2)C(7)C(8)C(9)N(3) changed to a boat conformation due to the tethering methylimino group. The two pyridine rings coordinate *cis* to each other and the dihedral angle between the two pyridine planes was 94.07°.

Complex **2** gave broad ^{1}H NMR spectra at room temperature but the spectra showed sharp signals at -10 °C. A new signal at δ 11.14 is assigned to the coordinated C=NH. The complex prepared from [$^2H_3$]acetonitrile in place of acetonitrile showed a spectrum which lacked the methyl signal at δ 2.48.§

The addition reaction of acetonitrile closely related to this has been reported by Riley and Busch.[3] The reaction conditions for preparation of acetonitrile adducts of macrocyclic tetraimine iron(ii) complexes preclude the use of nitriles other than acetonitrile. However, the isolation of **1** allows the reaction with other nitriles as solvents, in place of acetonitrile, *e*.g. [$^2H_3$]acetonitrile in this experiment. The reaction mechanism may be *via* nucleophilic attack of a carbanion formed at the central carbon of the 1,3-diimine moiety either to the acetonitrile coordinated to the apical position and activated by the iron(ii) centre as proposed by Riley *et al*. or to a bulk acetonitrile followed by coordination of imine nitrogen to the apical position. This can be resolved by the kinetics of this reaction. The use of a variety of nitriles for the preparation of iron(ii) complexes with this new class of pentadentate ligands are now under study.

Footnotes

† *Experimental procedure*: **1**; $Fe(ClO_4)_2\cdot6H_2O$ (8.02 g, 95%, 0.021 mol) was placed in a 250 ml Schrenck and a mixture of orthoethylformate (23 ml) and acetonitrile (46 ml) was added. The mixture was stirred at 50 °C overnight. $MeCOCH_2C(Me)=NHCH_2C_5H_4N$ (3.99 g, 0.021 mol) and 2-(aminomethyl)pyridine (2.16 g, 0.019 mol) were added successively. After the mixture was stirred for 2 h at 50 °C, the mixture was cooled and dehydrated diethyl ether was added. Pale-red crystals were obtained which were stored *in vacuo*. Yield, 6.97 g (0.11 mol), 53.8%.

2; five drops of triethylamine was added through a syringe to an acetonitrile (8 ml) solution of **1** (266 mg, 0.404 mmol). After stirring at room temp. for 2 h, the reaction mixture was concentrated to dryness. The remaining orange solid was dissolved in 5 ml of acetonitrile, thf (40 ml) was added and the separated orange crystals were collected and stored *in vacuo*. Yield, 235 mg (84.4%). Anal. Calc. for $C_{21}H_{26}Cl_2FeN_6O_8\cdot C_4H_8O$: C, 43.56; H, 4.97; N, 12.19. Found: C, 43.04; H, 4.79; N, 12.02%.

‡ *Crystal data* for **1** and **2**: reflections were collected on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), at T = 293 K to $2\theta_{max}$ = 55.0°. **1**; $C_{23}H_{29}Cl_2FeN_7O_8$, M = 658.28, triclinic, space group $P\bar{1}$, a = 12.361(3), b = 12.415(2), c = 10.472(2) Å, α = 94.68(1), β = 112.19(1), γ = 80.41(2)°, U = 1467.1(6) Å^3, Z = 2, D_c = 1.490 g cm^{-3}, $F(000)$ = 680, μ = 7.53 cm^{-1}. Data were corrected for absorption and extinction. $R_w = \{\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)\}^{1/2}$ = 0.055, $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ = 0.050 for 3399 reflections with $I/\sigma(I) > 3.0$.

2: $C_{25}H_{34}Cl_2FeN_6O_9$, M = 689.33. monoclinic, space group $P2_1/a$, a = 19.235(2), b = 16.044(3), c = 20.732(3) Å, β = 102.91(1)°, U = 6236(1) Å^3, Z = 8, D_c = 1.468 g cm^{-3}, $F(000)$ = 2864.00, μ = 7.13 cm^{-1}. Data were corrected for absorption and extinction. R_w = 0.068, R = 0.082 for 7115 reflections with $I/\sigma(I) > 3.0$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/368.

§ *Selected spectroscopic data*: **1**; ^{1}H NMR (CD_3CN, 298 K) δ 10.59 [C(1)H], 8.53[C(4)H], 8.26[C(2)H], 7.86[C(3)H], 6.35[C(6)H_2], 3.98[C(8)H_2], 2.61[C(16)H_3]. **2**; the HMQC and HMBC spectra (500 MHz) at -10 °C uniquely determined the ^{13}C and ^{1}H signals (δ): C(1), 152.51; C(2), 125.03; C(3), 138.90; C(4), 121.92; C(5), 165.70; C(6), 61.06; C(7); 176.96; C(8), 69.35; C(9), 177.78; C(10), 60.39; C(11), 165.13; C(12), 122.60; C(13), 139.19; C(14), 125.27; C(15), 156.01; C(16), 24.39; C(17), 24.28; C(18), 184.70; C(19), 29.15.

H(1), 7.10; H(2), 7.18; H(3), 7.82; H(4), 7.49; H(5), H(6), 5.24, 5.49 (AB); H(7), 5.66; H(8), H(9), 4.79, 5.33 (AB); H(10), 7.63; H(11), 8.02; H(12), 7.57; H(13), 9.03; H(14)–(16), 2.58; H(17)–(19), 2.40; H(20), 11.14; H(21)–(23), 2.48.

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