Observation of the Longest Fe–N(pyridine) Bond in an $Fe^{II}N_6$ Chromophore. Crystal Structure and ^1H Nuclear Magnetic Resonance Studies of $[FeL^2{}_2][ClO_4]_2$ [L^2 = 2-(3,5-dimethylpyrazol-1-ylmethyl)-6-(pyrazol-1-ylmethyl)pyridine]†

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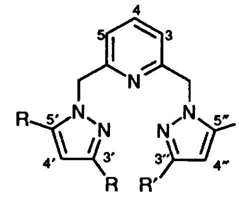
The X-ray structural and ^1H NMR spectral properties of a bis(ligand) iron(II) complex of a tridentate pyridylpyrazole ligand L^2 [L^2 = 2-(3,5-dimethylpyrazol-1-ylmethyl)-6-(pyrazol-1-ylmethyl)pyridine] have been studied. The complex $[FeL^2{}_2][ClO_4]_2$ crystallizes as yellow prisms in the monoclinic space group $P2_1/n$ with a = 14.122(3), b = 13.612(3), c = 18.393(4) Å, β = 99.11(3)°, Z = 4, R = 0.0518 and R' = 0.0634 for 6464 observed reflections. The Fe atom is bound to six nitrogen atoms from two tridentate (N_3) heterocyclic ligands. Considerable distortion is observed with the average Fe–N(pyridine) and Fe–N(pyrazole) distances being 2.274 and 2.173 Å respectively. These bond lengths are markedly longer than corresponding lengths for complexes of less sterically demanding ligands. As expected, the ligand molecules are not planar, the pyridyl and pyrazole rings being twisted relative to each other. The 3-methyl substituent induces a steric barrier to co-ordination and also greater inter-ligand repulsions and this is presumably responsible for the accessibility of the quintet state for Fe^{II}. The ^1H NMR spectral measurements in CD_3CN reveal that its solid-state structure is retained in solution.

The present work stems from our continued research interest [1,2] in the identification of the steric effect of methyl substituent(s) adjacent to donor atoms in groups of bis-ligated high-spin complexes of type $[ML_2]^{2+}$ (M = Fe^{II}, Co^{II} or Ni^{II}) using a new family of three tridentate pyridylpyrazole ligands.

The effect has been identified by investigating the trends in the energies of the ligand field spectral transitions,[1a,c,d] the M^{III}–M^{II} redox potentials (M = Mn, Fe or Co)[1a,b,d] and the temperature dependence of the spin-state properties of iron(II) complexes.[1e] Given the scarcity [1a,e,3–11] of high-spin bis(ligand) iron(II) complexes of pyridine-containing ligands the structural information on the complexes $[FeL^1{}_2]^{2+}$, $[FeL^2{}_2]^{2+}$ or $[FeL^3{}_2]^{2+}$ (all are high-spin at room temperature)[1a] would be of considerable interest to rationalize the chemical significance of the observed results.[1a,e] It is interesting that the latter two complexes are high spin even at low temperatures.[1e] Understandably, the metric parameters from the unsymmetrical complex $[FeL^2{}_2]^{2+}$ would be of most interest since here an opportunity exists for a comparison between the two different kinds of pyrazole rings in a given ligand, one with two methyl groups at the 3- and 5- positions and the other which is unsubstituted. Herein we describe the solid-state structure of $[FeL^2{}_2][ClO_4]_2$ as revealed from three-dimensional X-ray crystallographic analysis. The results of our investigation on the solution structure of this complex from ^1H NMR spectroscopic measurements are also reported.

Experimental

Synthesis.—The complex $[FeL^2{}_2][ClO_4]_2{\cdot}2H_2O$ was synthesized by using a literature method.[1a] The ^1H NMR spectrum was measured in CD_3CN on a Brüker WM-400 (400 MHz) NMR spectrometer. This was obtained as before:[1a] (CD_3CN, 298 K), δ 54.0 (2 H, $H^{3,5}$), 51.8 (1 H, $H^{4'}$ or $H^{4''}$), 48.8 (1 H, $H^{4'}$ or $H^{4''}$), 47.0 (2 H, $H^{3,5}$), 46.4 (1H, $H^{4'}$ or $H^{4''}$), 45.8 (1 H, $H^{4'}$ or $H^{4''}$), 44.0 (6 H, $Me^{3''}$), 30.5 (1 H, $H^{5'}$), 29.5 (3 H, $Me^{5''}$), 28.8 (2 H, $H^{3'}$), 26.2 (3 H, $Me^{5''}$), 25.2 (1 H, $H^{5'}$), 11.8 (1 H, H^4), 9.8 (1 H, H^4), −16.5 (1 H, CH_2), −18.8 (1 H, CH_2), −25.0 (1 H, CH_2), −31.0 (1 H, CH_2), −47.0 (1 H, CH_2), −56.8 (1 H, CH_2), −65.0 (1 H, CH_2) and −76.0 (1 H, CH_2).



L^1 R = R′ = H
L^2 R = H; R′ = Me
L^3 R = R′ = Me

Crystal Structure Determination and Refinement.—Crystals of $[FeL^2{}_2][ClO_4]_2$ suitable for diffraction were obtained by slow evaporation from an aqueous methanolic solution of the microcrystalline complex $[FeL^2{}_2][ClO_4]_2{\cdot}2H_2O$. A yellow rectangular parallelopiped crystal was mounted on a glass fibre. Diffraction measurements (Howard University) were made at 173 K using a Siemens P4/RA diffractometer with a rotating anode generator (highly oriented graphite crystal as monochromator).

The unit-cell dimensions were obtained from a least-squares refinement of 25 strong, machine-centred reflections. All experimental parameters used are given in Table 1. Absorption corrections were not applied as psi scans revealed very little variation in intensity (< 5%).

Atomic scattering factors and corrections for anomalous

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

dispersion effects were taken from ref. 12. Of 10 863 measured reflections, 9025 were independent (R_{int} = 2.17%), and 6464 were considered 'observed' with $F_o > 4\sigma(F_o)$ and were used in all subsequent least-squares refinements.

The structure was solved by direct methods and refined using full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0004(F_o)^2]$. The positions of the hydrogen atoms were computed using a riding model with fixed isotropic *U*. All calculations were performed using the SHELXTL PLUS program (PC version).[13]

Table 1 Summary of X-ray diffraction data for $[FeL^2{}_2][ClO_4]_2$ at 173 K

Formula	$C_{30}H_{34}Cl_2FeN_{10}O_8$
M	789.41
Crystal dimensions/mm	0.5 × 0.5 × 0.4
Crystal system	Monoclinic
a/Å	14.122(3)
b/Å	13.612(3)
c/Å	18.393(4)
β/°	99.11(3)
U/Å³	3491(13)
Radiation	Mo-Kα (λ = 0.71073 Å)
Space group	$P2_1/n$
Z	4
$D_m(D_c)$/g cm^{-3}	1.49 (1.502)
μ/cm^{-1}	6.49
Scan type	ω
2θ range/°	3.5–60
Index ranges, *hkl*	−1 to 19, −1 to 18, −24 to 24
Standard reflections	3 Measured every 97
No. of observed data	6464 [$F > 4.0\sigma(F)$]
F(000)	1632
No. of variables	486
Data: parameter ratio	13.3 : 1
Largest and mean Δ/σ	0.468, 0.025
$R(F_o)$[a]	0.0518
$R'(F_o)$[b]	0.0634
Goodness of fit[c]	1.48
Maximum, minimum peak in final difference map/e Å^{-3}	0.45, −0.57

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)]^{\frac{1}{2}}$. [c] Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$, N_o and N_p are the number of observations and parameters.

One of the two perchlorate ions was found to be disordered. For this approximately tetrahedral perchlorate ion, the apical oxygen atom was unique, but the remaining three oxygens were disordered over two positions, with a major and minor component. In addition to refining positional and thermal parameters for each oxygen atom in the groups, a multiplicity factor for each set of the three disordered oxygen atoms was refined so that the total multiplicity for both sites was unity.

Atomic coordinates are listed in Table 2 and selected bond distances and angles are reported in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Solid-state Structure.—Initially diffraction measurements were made at 296 K. However, as the quality of the data set was rather poor and both the perchlorates were severely disordered, we have collected the present data at 173 K.

A perspective view of the discrete complex cation and the atom-labelling scheme are shown in Fig. 1. The six nitrogen atoms of the two L² ligands co-ordinate to the iron atom and form a distorted octahedron about it. The ligands adopt a *mer* configuration about the metal atom so that the complex cation has no overall symmetry. This kind of configuration, similar to that found in many other related systems,[3f] arises presumably because it leads to reduced inter-ligand interactions. Gross distortions from octahedral symmetry are evident in the FeN_6 core geometry with Fe–N distances varying from 2.156(2) to 2.289(2) Å and angular deviations from octahedral values (Table 3). There are two types of heterocyclic nitrogen donor atoms: four pyrazole nitrogens and two pyridine nitrogens. These two types are associated with different Fe–N bond

Table 2 Atomic coordinates (× 10⁵) for $[FeL^2{}_2][ClO_4]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	29 509(3)	25 488(3)	6 600(2)	C(22a)	26 691(24)	4 123(27)	−11 373(18)
Cl(1)	77 130(7)	25 578(8)	20 599(6)	C(11b)	47 644(21)	26 095(24)	−2 396(17)
Cl(2)	21 521(6)	73 093(6)	10 602(5)	C(14b)	51 472(26)	16 208(27)	23(21)
O(11)	71 902(31)	24 646(54)	26 356(25)	C(4b)	3 967(23)	40 349(27)	−7 026(17)
O(12)	82 082(43)	16 282(37)	19 893(42)	C(21a)	27 340(22)	13 713(25)	−8 784(16)
O(13)	84 747(28)	31 964(30)	21 724(27)	C(3b)	7 389(25)	49 160(28)	−9 086(18)
O(14)	70 510(37)	26 587(57)	13 783(27)	C(13b)	44 902(23)	40 108(26)	−8 309(18)
O(21)	15 823(20)	70 606(21)	16 145(17)	C(21b)	15 226(22)	21 166(23)	18 215(17)
O(22)	16 552(24)	80 082(27)	5 658(21)	C(1b)	22 812(21)	44 504(21)	−3 041(15)
O(23)	23 327(32)	64 509(23)	6 716(19)	C(14a)	18 478(23)	45 357(23)	16 007(18)
O(24)	30 299(18)	77 422(20)	14 029(16)	C(23a)	26 443(22)	−1 733(25)	−5 361(17)
N(22b)	16 609(16)	22 106(18)	11 220(13)	C(2b)	16 995(25)	51 338(25)	−7 173(16)
N(1b)	19 646(16)	35 799(17)	−976(12)	C(2a)	52 653(22)	10 074(23)	21 927(17)
N(1a)	38 315(16)	14 234(16)	13 751(12)	C(12a)	34 102(24)	45 403(23)	25 496(16)
N(12b)	41 051(17)	30 774(18)	859(13)	C(3a)	50 532(25)	214(24)	21 187(17)
N(22a)	27 519(18)	13 805(18)	−1 442(12)	C(13a)	42 478(24)	40 194(24)	26 262(15)
N(12a)	33 193(16)	35 245(16)	15 852(12)	C(11a)	28 456(22)	42 188(20)	19 069(16)
N(11a)	41 795(16)	34 116(17)	20 433(12)	C(6b)	33 214(21)	46 793(21)	−463(17)
N(21a)	27 016(18)	4 237(17)	523(13)	C(5a)	36 187(21)	4 561(20)	13 111(15)
N(21b)	7 773(17)	22 778(18)	7 202(15)	C(7a)	27 055(22)	1 653(21)	8 219(15)
N(11b)	39 573(17)	39 496(18)	−2 819(13)	C(4a)	42 177(24)	−2 535(22)	16 733(16)
C(15b)	44 452(33)	48 903(32)	−13 260(23)	C(6a)	49 094(20)	27 598(21)	18 437(16)
C(15a)	51 147(30)	40 565(34)	32 025(19)	C(5b)	10 170(20)	33 768(23)	−2 990(15)
C(22b)	5 456(25)	21 081(28)	18 636(21)	C(1a)	46 403(19)	16 881(20)	18 167(15)
C(12b)	50 153(24)	31 696(28)	−8 077(19)	O(11′)	71 877(116)	35 082(123)	21 891(85)
C(7b)	6 594(21)	23 995(23)	−731(17)	O(14′)	75 790(148)	24 035(136)	13 452(107)
C(23b)	963(24)	22 164(26)	11 545(21)	O(12′)	76 090(139)	19 402(132)	25 662(103)

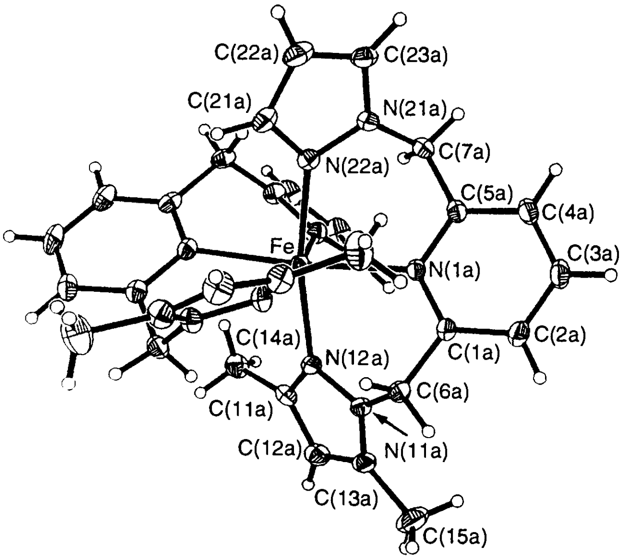

Fig. 1 Perspective view of $[FeL^2_2][ClO_4]_2$ showing the atom labelling scheme

Table 3 Selected intramolecular bond lengths (Å) and bond angles (°) for $[FeL^2_2][ClO_4]_2$

Fe–N(1a)	2.259(2)	Fe–N(1b)	2.289(2)	Fe–N(22a)	2.160(2)
Fe–N(22b)	2.178(3)	Fe–N(12a)	2.156(2)	Fe–N(12b)	2.199(3)

N(22a)–Fe–N(22b)	94.9(1)	N(1a)–Fe–N(22a)	84.2(1)
N(12a)–Fe–N(22b)	86.2(1)	N(1a)–Fe–N(22b)	92.7(1)
N(1a)–Fe–N(12a)	85.2(1)	N(1a)–Fe–N(12b)	96.9(1)
N(12a)–Fe–N(22a)	169.4(1)	N(1b)–Fe–N(22a)	91.9(1)
N(12a)–Fe–N(1b)	98.6(1)	N(12b)–Fe–N(22a)	86.4(1)
N(1a)–Fe–N(1b)	174.9(1)	N(12b)–Fe–N(22b)	170.4(1)
N(12a)–Fe–N(12b)	94.2(1)	N(1b)–Fe–N(22b)	84.3(1)
N(1b)–Fe–N(12b)	86.2(1)	Fe–N(22b)–N(21b)	122.0(2)
Fe–N(1b)–C(5b)	121.3(2)	Fe–N(1b)–C(1b)	121.0(2)
Fe–N(1a)–C(1a)	120.5(2)	Fe–N(1a)–C(5a)	121.0(2)
Fe–N(22a)–N(21a)	122.1(2)	Fe–N(12b)–N(11b)	117.1(2)
Fe–N(12b)–C(11b)	132.6(2)	Fe–N(12a)–C(11a)	134.7(2)
Fe–N(22b)–C(21b)	130.8(2)	Fe–N(22a)–C(21a)	132.3(2)
Fe–N(12a)–N(11a)	119.7(2)		

distances: the pyrazole nitrogens are more closely bound, while the pyridine nitrogens are about 4% more distant. The Fe–N(pyridine) and Fe–N(pyrazole) bond distances are reasonable for iron(II) in a high-spin electronic configuration and agrees well with earlier results for six-co-ordinate iron(II) complexes with heteroaromatic nitrogen atoms (see below). It has previously been observed that the donor atom of a five-membered heterocycle is closer to the metal atom than that of a six-membered heterocycle in a mixed chelate ligand.[3c,3e] Comparison with the complexes of N^1-(pyridin-2-yl)-3,5-dimethylpyrazole[3e] is particularly relevant since in these and in the present complex there is a methyl group adjacent to the donor atom of the five-membered heterocycle. Despite the barrier to co-ordination expected from this group, the metal–donor atom distance is relatively short and the effect is most marked in the present complex where the average difference [Fe–N(pyridine) − (Fe–N(pyrazole)] is 0.101 Å. The shortness of the Fe–N(pyrazole) bond is consistent with the fact that the metal atom is out of the plane of the pyridine ring (see below). Of particular interest are the iron–pyridine bond lengths of 2.259(2) and 2.289(2) Å. The average Fe–N(pyridine) bond distance encountered here is the longest observed for structurally characterized high-spin six-co-ordinate bis(chelates) of heteroaromatic nitrogen donors of iron(II) (Table 4).

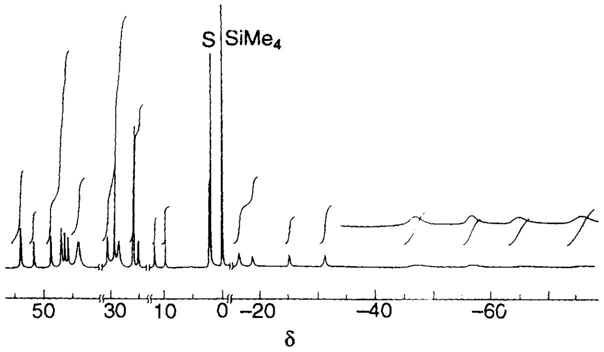

Fig. 2 400 MHz ^1H NMR spectrum of $[FeL^2_2][ClO_4]_2{\cdot}2H_2O$ in CD_3CN at 300 K (solvent peak indicated by S)

The pyridine and pyrazole rings are each planar to within 0.004 and 0.003 Å respectively. The two pyridine ring mean planes are tilted to each other by an angle of 27.2°. The two pyrazole mean planes of each ligand make an angle of 60.3 and 68.4° to each other. The pyridine mean plane is tilted to adjacent pyrazole rings within a ligand at angles of 48.2 and 59.1° and 59.6 and 59.7°. Thus the six-membered chelate rings exist in boat conformations. A similar chelate ring conformation was observed in the crystal structure of $[NiL^1_2][ClO_4]_2$.[16]

Solution-state Structure by ^1H NMR Spectroscopy.—The solution structure of $[FeL^2_2]^{2+}$ has been examined using ^1H NMR spectroscopy. An immediate question is whether or not the solid-state structure is retained in solution.

Analysis of the spectra of $[FeL^1_2]^{2+}$ and $[FeL^3_2]^{2+}$ in CD_3CN has been given earlier.[1a] The spectrum of $[FeL^2_2][ClO_4]_2{\cdot}2H_2O$ in CD_3CN is shown in Fig. 2. Assignments of the resonances are made by a combination of the expected behaviour for paramagnetic complexes,[17,18] integrated area ratios and comparison with the spectra of $[FeL^1_2]^{2+}$ and $[FeL^3_2]^{2+}$.[1a] As the symmetry of the complex $[FeL^2_2]^{2+}$ is very low (see crystal structure) due to the unsymmetrical nature of L^2, almost all the protons are expected to be magnetically non-equivalent. A large number of peaks are observed (Fig. 2), justifying our expectation. The most important proton resonances to provide information on the solution-state co-ordination geometry of this complex are the methylene protons. The eight upfield resonances (of which four are very broad) are assigned to axial and equatorial protons of the four methylene groups. Thus the four protons present in both arms of each ligand are not interconverting on the NMR time-scale, otherwise a singlet would have resulted for each methylene group. The four comparatively sharper methylene proton resonances are due to the CH_2 protons more distant from the iron(II) centre and the other four are due to those which are near the metal centre.

Thus ^1H NMR spectral studies on the present complex neatly demonstrate the retention of the solid-state structure in solution.

Conclusion

A fairly distorted octahedral co-ordination is observed for $[FeL^2_2][ClO_4]_2$ from a single-crystal X-ray analysis. This arises from the steric crowding between the methyl groups near the donor site. The average Fe–N(pyridine) bond length for this complex is the longest among known bis- or tris-(ligand) iron(II) complexes with FeN_6 co-ordination. The ^1H NMR studies demonstrate that the solid-state structure is retained in solution. To the best of our knowledge the present structure is the first amongst this kind of high-spin bis(ligand) iron(II) complexes of the pyridine containing heterocyclic ligands where the spin state is dictated by the steric effect of methyl substituents near the

Table 4 Comparison of Fe–N(pyridine) and Fe–N(pyrazole) distances in mononuclear high-spin $Fe^{II}N_6$ complexes

	Fe–N (av) Å		
Complex[a]	Fe–N(pyridine)	Fe–N(pyrazole)	Ref.
$[FeL^2{}_2][ClO_4]_2$	2.274	2.173	This work
$[Fe(dmphen)(NCS)_2]\cdot 0.25H_2O$	2.275		5
$[Fe(py)_6]^{2+}$	2.258		6
$[Fe(py)_4(NCS)_2]$	2.255		7
$[FeL^4{}_2]$		2.246	14
$[FeL^5{}_2]$		2.172	15
$[Fe(mphen)_3]^{2+}$	2.208		3(*b*)
$[FeL^6{}_2]X_2\cdot$solv			
X = Br[b], solv = EtOH	2.223		8(*a*)
X = Cl, solv = MeOH[c,d]	2.198		8(*b*)
X = Cl, solv = MeOH[e]	2.210		8(*c*)
X = Cl, solv = EtOH[e]	2.209		8(*d*)
X = I[e]	2.205		8(*e*)
$[Fe(mbipy)_3]^{2+}$	2.209		3(*f*)
$[Fe(phen)_2(NCS)_2]$	2.206		9
$[FeL^7(NCS)_2]$	2.222		10
$[FeL^8{}_3]^{2+}$	2.199		3(*c*)
$[Fe(bipy)(NCS)_2]$	2.170		11
$[FeL^9{}_3]^{2+}$	2.064	1.984	3(*e*)

[a] Ligand abbreviations: dmphen = 2,9-dimethyl-1,10-phenanthroline, py = pyridine, L^4 = hydrotris(3-phenylpyrazol-l-yl)borate, L^5 = hydrotris(3,5-dimethylpyrazol-l-yl)borate, mphen = 2-methylphenanthroline, L^6 = 2-methylpyridylamine, mbipy = 6-methyl-2,2′-bipyridine, phen = 1,10-phenanthroline, L^7 = 2,2′-bi(2-thiazoline), L^8 = 4-methyl-(2-pyridin-2-yl)thiazole, bipy = 2,2′-bipyridine, L^9 = *N*^{1}-(pyridin-2-yl)-3,5-dimethylpyrazole. [b] At 215 K. [c] At 227 K. [d] 84% high spin. [e] At room temperature.

donor site. The X-ray structural results presented here underpin the chemical significance of the observed properties of these systems.[1a,e]

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