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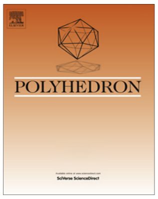

Iron(II) complexes of 2,6-di(1-alkylpyrazol-3-yl)pyridine derivatives – The influence of distal substituents on the spin state of the iron centre

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ABSTRACT

2,6-Di(1-methyl-pyrazol-3-yl)pyridine (L^{Me}), 2,6-di(1-allyl-pyrazol-3-yl)pyridine (L^{All}), 2,6-di(1-benzyl-pyrazol-3-yl)pyridine (L^{Bz}) and di(1-*iso*propyl-pyrazol-3-yl)pyridine (L^{iPr}) have been synthesized by alkylation of deprotonated di{1*H*-pyrazol-3-yl}pyridine (3-bpp), and converted to salts of the corresponding $[Fe(L^R)_2]^{2+}$ complexes (R = Me, All, Bz and *i*Pr). Crystal structures of $[Fe(L^{Me})_2]X_2$ ($X^- = BF_4^-$, ClO_4^- and PF_6^-), $[Fe(L^{All})_2][BF_4]_2$, $[Fe(L^{Bz})_2][BF_4]_2$ and $[Fe(L^{iPr})_2][PF_6]_2$ have been determined at 150 K. All of these contain high-spin iron centres except $[Fe(L^{Me})_2][BF_4]_2{\cdot}xH_2O$, which is predominantly low-spin at that temperature. All the complexes are high-spin between 5 and 300 K as solvent-free bulk powders, and are also high-spin in $(CD_3)_2CO$ solution between 193 and 293 K. This was unexpected, since the parent complex $[Fe(3\text{-bpp})_2]^{2+}$ undergoes spin-crossover in the same solvent with $T_{½} = 247$ K [40]. The high-spin nature of the $[Fe(L^R)_2]^{2+}$ complexes in solution must reflect a subtle balance of steric and electronic factors involving the ligand 'R' substituents.

1. Introduction

The chemistry of spin-crossover complexes [1–3] continues to be heavily studied, because of their potential applications as switchable components in memory and display devices [4], in nanoscience [2] and in MRI contrast agents [5]. A class of compound that has been heavily used in spin-crossover research during the past ten years are iron(II) complexes of the isomeric 2,6-di(pyrazolyl)pyridine ligands, 1-bpp and 3-bpp (Scheme 1) [6,7]. The 1-bpp ligand framework can be substituted at every position of its pyrazole and pyridine rings [7]. Substitution at the pyridine ring allows functional groups to be included at the periphery of the $[Fe(1\text{-bpp})_2]^{2+}$ centre without significantly perturbing the iron centre. This approach has afforded multifunctional spin-crossover complexes [8], coordination polymers of $[Fe(1\text{-bpp})_2]^{2+}$ centres [9], and complexes with tether groups for deposition on surfaces [10]. In contrast, substituents at the pyrazole groups allow for steric and electronic control of the spin-state properties of a $[Fe(1\text{-bpp})_2]^{2+}$ complex, so its spin-crossover properties can be modified in a rational way [7]. The synthetic versatility of $[Fe(1\text{-bpp})_2]^{2+}$ is unique among the commonly used compounds in the field of spin-crossover.

The coordination chemistry of substituted 3-bpp derivatives is less developed by comparison, because of the poorer availability of suitable synthetic precursors. 3-bpp ligands derivatised at *N*1 and *C*5 of the pyrazole rings are well-established, and have been employed in luminescent complexes [11–13], in catalysis [14–16], in hydrometallurgical applications [17] and in self-assembly reactions [18,19]. However, although $[Fe(3\text{-bpp})_2]^{2+}$ itself is a versatile spin-crossover compound [6], the application of substituted 3-bpp ligands to spin-crossover chemistry has only recently been investigated, by us [20] and by Aromí co-workers [21].

We describe here the first investigation of iron complexes of 3-bpp derivatives that are disubstituted at the pyrazole *N*1 positions. These are analogues of 1-bpp ligands bearing substituents at the pyrazole *C*3 sites, where the pyrazole substitutents are known to have a strong bearing on the spin-state properties of a coordinated iron centre [6]. Four 3-bpp derivatives have been investigated in this work: 2,6-di(1-methylpyrazol-3-yl)pyridine (L^{Me}), 2,6-di(1-allylpyrazol-3-yl)pyridine (L^{All}), 2,6-di(1-benzylpyrazol-3-yl)pyridine (L^{Bz}) and 2,6-di(1-*iso*propylpyrazol-3-yl)pyridine (L^{iPr}) (Scheme 1). Some noble metal complexes of L^{Me} [13] and L^{All} [16] have been reported before but their iron complexes have not yet been investigated, while L^{Bz} and L^{iPr} are new ligands to our knowledge. We were particularly interested in salts of $[Fe(L^{Me})_2]^{2+}$ since the $Fe[BF_4]_2$ complex of the equivalent 1-bpp derivative, 2,6-di(3-methylpyrazol-1-yl)pyridine (Me_2-1-bpp),

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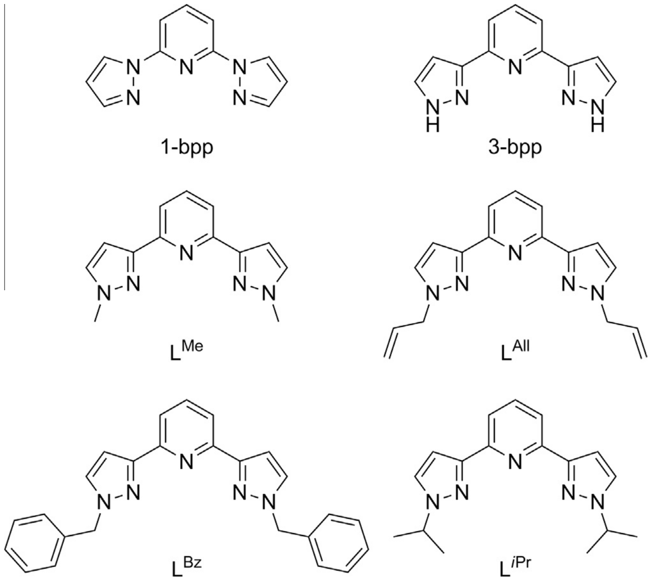

Scheme 1.

exhibits an unusually low thermal spin-transition temperature for a complex of this type which leads to unique light-induced spin-crossover properties [22]. We were therefore keen to see whether salts of $[Fe(L^{Me})_2]^{2+}$ exhibit comparable effects.

2. Experimental

Unless otherwise stated, all manipulations were carried out in air using reagent-grade solvents. 2,6-Di(pyrazol-3-yl)pyridine (3-bpp) [23], 2,6-di(1-methylpyrazol-3-yl)pyridine (L^{Me}) [13] and 2,6-di(1-allylpyrazol-3-yl)pyridine (L^{All}) [16] were prepared by literature methods, while all other reagents and solvents were used as supplied.

2.1. Synthesis of 2,6-di(1-benzylpyrazol-3-yl)pyridine (L^{Bz})

2,6-*Bis*(pyrazol-3-yl)pyridine (2.00 g, 9.5 mmol) and lithium hydride (0.22 g, 28.4 mmol) were suspended in dry THF, in the presence of benzyl bromide (4.86 g, 28.4 mmol). The mixture was then heated at reflux for 44 h under a nitrogen atmosphere. The resultant white precipitate was removed via filtration and washed with water. The solid was then recrystallised from chloroform and dried *in vacuo*. Yield 1.67 g, 45%. EI HR mass spectrum: m/z 391.1795 ($[L^{Bz}]^+$; calcd for $C_{25}H_{21}N_5$ m/z 391.1797). ^{1}H NMR (CDCl$_3$) δ5.31 (br s, 4H, CH_2), 7.01 (br s, 2H, Pz H^4), 7.18–7.38 (br m, 10H, C$_6H_5$), 7.40 (d, 2.3 Hz, 2H, Pz $H^{5'}$), 7.75 (t, 7.5 Hz, 1H, Py H^4), 7.86 (br s, 2H, Py $H^{3/5}$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ56.2 (2C, CH$_2$), 105.2 (2C, Pz C^4), 118.6 (2C, Py $C^{3/5}$), 127.5 (Ph $C^{2/6}$), 128.0 (Ph $C^{3/5}$), 128.8 (Ph C^4), 130.9 (2C, Pz C^5), 136.4 (2C, Ph C^1), 137.3 (1C, Py C^4), 151.7 and 152.0 (both 2C, Py $C^{2/6}$ and Pz C^3).

2.2. Synthesis of 2,6-di(1-isopropylpyrazol-3-yl)pyridine (L^{iPr})

The same method as described for L^{Bz} was followed, using 2-iodopropane (4.83 g, 28.4 mmol). After 72 h at reflux under a nitrogen atmosphere, the resultant white precipitate was collected, washed with water and dried *in vacuo*. The product was employed without further purification. Yield 2.67 g, 95%. EI HR mass spectrum: m/z 296.1874 ($[HL^{iPr}]^+$; calcd for $C_{17}H_{22}N_5$ m/z 296.1870). ^{1}H NMR ({CD$_3$}SO) δ1.47 (d, 6.6 Hz, 12H, CH{CH_3}$_2$), 4.57 (sept, 6.6 Hz, 2H, CH{CH$_3$}$_2$), 6.92 (d, 2.1 Hz, 2H, Pz H^4), 7.83 (s, 2H, Pz H^5), 7.84 (s, 3H, Py H^{3-5}). ^{13}C{^{1}H} NMR ({CD$_3$}SO): δ22.2 (4C, CH{CH$_3$}$_2$), 54.3 (2C, CH{CH$_3$}$_2$), 104.0 (2C, Pz C^4), 119.3 (2C, Py $C^{3/5}$), 128.9 (2C, Pz C^5), 139.0 (1C, Py C^4), 149.6 and 151.0 (both 2C, Py $C^{2/6}$ and Pz C^3).

2.3. Synthesis of the complexes

The same basic method, as described here for $\mathbf{1[BF_4]_2}$, was followed for all the complexes in this study. Iron(II) tetrafluoroborate hexahydrate (0.14 g, 0.4 mmol) was added to a stirred solution of L^{Me} (0.20 g, 0.8 mmol) in nitromethane (15 mL) and the resulting yellow solution was stirred for a further 30 min. Diethyl ether was then added until a yellow precipitate formed which was collected via filtration. The product was then recrystallised from methanol/diethyl ether to give a yellow crystalline solid. The same method, using the equivalent quantities of the appropriate ligand and metal salt, yielded the other complexes. Recrystallised yields ranged from 38% to 70%. *Caution!* Although we have experienced

Table 1
Experimental details for the single crystal structure determinations in this work.

	$\mathbf{1[BF_4]_2}\cdot x\mathrm{H_2O}$	$\mathbf{1[ClO_4]_2}$	$\mathbf{1[PF_6]_2}$	$\mathbf{2[BF_4]_2}$	$\mathbf{3[BF_4]_2}$	$\mathbf{4[PF_6]_2}\cdot 2\mathrm{CH_3CN}$
Formula	$C_{26}H_{28}B_2F_8FeN_{10}O$	$C_{26}H_{26}Cl_2FeN_{10}O_8$	$C_{26}H_{26}F_{12}FeN_{10}P_2$	$C_{34}H_{34}B_2F_8FeN_{10}$	$C_{50}H_{42}B_2F_8FeN_{10}$	$C_{38}H_{48}F_{12}FeN_{12}P_2$
M_r	726.05	733.32	824.36	812.18	1012.41	1018.67
Crystal system	monoclinic	trigonal	monoclinic	cubic	orthorhombic	monoclinic
Space group	$C2/c$	$R32$	$C2/c$	$I\bar{4}3d$	$Pbca$	$P2_1/n$
a (Å)	17.1632(16)	18.6378(12)	34.124(3)	22.8650(18)	15.4334(17)	20.494(2)
b (Å)	20.9906(19)	–	12.3128(11)	–	14.0656(17)	23.257(3)
c (Å)	19.1771(17)	24.3461(14)	17.6817(17)	–	43.884(5)	20.609(2)
β (°)	96.605(5)	–	114.441(6)	–	–	101.271(6)
V (Å^3)	6863.0(11)	7324.0(8)	6763.4(11)	11954.0(16)	9526.3(19)	9633.3(19)
Z	8	9	8	12	8	8
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
ρ_{calc} (g cm^{-3})	1.405	1.496	1.619	1.354	1.412	1.405
μ (mm^{-1})	0.520	0.690	0.643	0.454	0.396	0.468
Measured reflections	37795	23056	62406	87527	162266	524427
Independent reflections	6723	4972	10895	2127	11794	23521
R_{int}	0.056	0.030	0.082	0.041	0.049	0.047
Observed reflections [$I > 2\sigma(I)$]	4552	4218	7634	1847	9529	17909
Data, restraints, parameters	6723, 40, 460	4972, 14, 216	10895, 0, 464	2127, 25, 162	11794, 0, 640	23521, 102, 1282
$R_1(I > 2\sigma(I))$[a], wR_2(all data)[b]	0.085, 0.297	0.061, 0.171	0.048, 0.132	0.048, 0.136	0.045, 0.127	0.063, 0.188
GOF	1.041	1.058	1.023	1.108	1.024	1.100
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.58, 1.05	−0.55, 0.68	−0.62, 0.78	−0.21, 0.36	−0.76, 1.00	−0.74, 0.94
Flack parameter	–	0.00(3)	–	−0.02(3)	–	–

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|Fo$.

[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.