

Rapid Communication

A low-spin carboxyl-bonded iron(III) complex

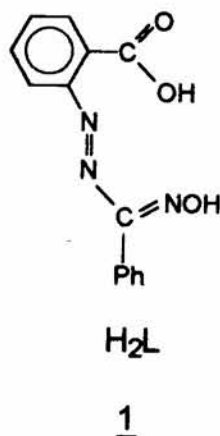
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The ligand $\text{HON}=\text{C}(\text{Ph})\text{N}=\text{N}-\text{C}_6\text{H}_4\text{CO}_2\text{H}$ (H_2L) has afforded the low-spin ($S=1/2$) iron(III) complex, $\text{Et}_4\text{N}[\text{Fe}(\text{PhL})_2]$ which has been structurally characterised revealing the presence of *cis*- FeN_4O_2 coordination sphere. Carboxyl-bonded low-spin iron(III) species are very rare. Spin-pairing contracts metal radius, the Fe-N and Fe-O lengths being significantly shorter than those in representative high-spin complexes.

Carboxyl coordination is a very common feature in the chemistry and biochemistry of trivalent iron¹⁻⁴. Virtually all the known species are high-spin ($S=5/2$) consistent with the large spin-pairing energy⁵ of iron(III) ($3d^5$) and the low ligand-field strength of the carboxyl group⁶. Herein we describe an example of the unusual low-spin ($S=1/2$) situation achieved with the help of the new ligand 1, abbreviated as H_2L .



Experimental

EPR spectra were measured on a Varian E-109C spectrometer. Magnetic susceptibility was determined with a Model 155 PAR vibrating sample magnetometer. X-ray structure determination

Table 1—Atomic coordinates ($\times 10^4$) for $\text{Et}_4\text{N}[\text{Fe}(\text{PhL})_2]$

	x	y	z
Fe	0	2090(2)	7500
O(1)	-962(13),	1045(7)	6447(12)
O(2)	1703(11)	3456(7)	8980(11)
O(3)	1020(10)	2712(6)	7987(9)
N(1)	-774(12)	2093(9)	8726(11)
N(2)	-1483(13)	1622(8)	8784(11)
N(3)	-924(15)	1389(8)	7242(14)
C(1)	972(17)	3078(10)	8796(16)
C(2)	57(19)	3046(9)	9505(12)
C(3)	104(22)	3503(9)	10295(15)
C(4)	-666(17)	3513(11)	10992(18)
C(5)	-1492(17)	3071(9)	10960(15)
C(6)	-1545(16)	2594(9)	10211(14)
C(7)	-742(15)	2589(9)	9499(14)
C(8)	-1610(17)	1204(10)	8004(16)
C(9)	-2324(16)	640(10)	8071(16)
C(10)	-2672(16)	442(11)	9001(16)
C(11)	-3329(16)	-111(12)	9087(18)
C(12)	-3676(16)	-415(11)	8265(18)
C(13)	-3347(17)	-236(11)	7348(19)
C(14)	-2664(15)	294(10)	7222(14)

was done on a crystal of dimension $0.21 \times 0.17 \times 0.15 \text{ mm}^3$ with the help of a Nicolet R3m/V diffractometer (MoK_α radiation, $\lambda=0.71073 \text{ \AA}$) using the SHELXTL-PLUS program⁷. Crystal data are: crystal system, orthorhombic; space group, *Pbcn*; $a = 12.709(8) \text{ \AA}$, $b = 20.14(2) \text{ \AA}$, $c = 13.428(12) \text{ \AA}$, $V = 3436(5) \text{ \AA}^3$; $Z = 4$; $R = 10.01\%$; $R_w = 7.18\%$. Data were collected in the 2θ range $3-45^\circ$ and 682 reflections with $I > 2\sigma(I)$ were used for structure solution employing direct methods. The crystal was relatively weakly diffracting and due to paucity of observed data, only the iron atom was made anisotropic. The hydrogen atoms were added at calculated positions. Coordinates of non-hydrogen atoms of the FeL_2^- anion are given in Table 1. Further details can be had from the author (AC).

The synthesis of the ligand H_2L and the complex $\text{Et}_4\text{N}[\text{FeL}_2]$ are outlined in the text and details will be given elsewhere. Analytical data, found (calc.) are as follows: for H_2L : C, 62.54(62.45); H, 4.21(4.09); N, 15.52(15.61) and for $\text{Et}_4\text{N}[\text{FeL}_2]$: C, 60.10(60.04); H, 5.15(5.28); N, 13.71(13.62).

Results and discussion

The reaction of H_2L with iron(III) chloride in methanol containing Et_4NCl afforded pink-co-

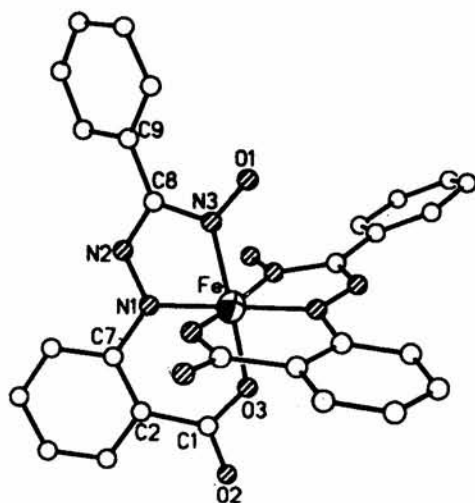


Fig. 1—Perspective view of the anion of $\text{Et}_4\text{N}[\text{Fe}(\text{PhL})_2]$. Selected distances (\AA) and angles ($^\circ$); Fe–N(1), 1.918(15), Fe–N(3), 1.869(18), Fe–O(3), 1.917(13), N(1)–Fe–N(1A), 179.7(4); O(3)–Fe–N(3), 169.0(7)

loured $\text{Et}_4\text{N}[\text{FeL}_2]$ in excellent yields. The ligand H_2L was synthesised by converting diazotised anthranilic acid to 2-hydrazinobenzoic acid which was reacted with benzaldehyde furnishing the corresponding hydrazone. The latter was nitrosated⁸ with *n*-butylnitrite affording yellow coloured H_2L in good yield (50%).

The room temperature magnetic moment of the complex is $1.92 \mu_{\text{B}}$ corresponding to the idealised f_2^2 ($S = 1/2$) configuration. Upon decreasing the temperature the moment varies only slightly (250 K, $1.91 \mu_{\text{B}}$; 200 K, $1.89 \mu_{\text{B}}$; 150 K, $1.86 \mu_{\text{B}}$; 90 K, $1.82 \mu_{\text{B}}$) as expected for the low-spin d^5 configuration^{9,10}. In frozen (77K) dimethylformamide-toluene glass $\text{Et}_4\text{N}[\text{FeL}_2]$ exhibits a well-resolved rhombic EPR spectra (g values: 2.173, 2.127, 1.997) consistent with the observed geometry (C_2 , see below) of the coordination sphere.

The X-ray structure of the complex anion FeL_2^- is shown in Fig. 1 and selected bond parameters are given in the legend.

Two tridentate ligands bind the metal in the hexadentate N_4O_2 fashion utilising pairs of oximate-N, azo-N and carboxyl-O atoms. The relative orientations within the pairs are *cis*, *trans* and *cis* respectively. The metal centre lies on crystallographic two-fold axis making the two meridional halves of the molecule equivalent.

The FeN_4O_2 coordination sphere is severely distorted from ideal octahedral geometry. The angles at the metal centre between *cis*-positioned

donor pairs span the range $80.8(8)^\circ$ – $99.5(8)^\circ$ and those between *trans*-positioned pairs are $169.0(7)^\circ$ and $179.7(4)^\circ$. The five-membered azo-oxime chelate ring, FeN_3C , is excellently planar with mean deviation of 0.01\AA . The six-membered chelate ring, FeC_3NO , is also planar with mean deviation of 0.07\AA .

Spin-pairing is expected to decrease metal radius^{11,12}. This indeed happens in FeL_2^- . Thus the Fe–O, Fe–N (oxime) and Fe–N (azo) lengths are 1.917(13), 1.869(18) and 1.918(15) \AA respectively compared to the expected¹³ high-spin values of 2.0, 2.1 and 2.1 \AA respectively.

In FeL_2^- , the azo oxime chelation ensures spin-pairing^{8,14} while carboxylate coordination stabilises the trivalent state. The only known carboxyl coordinated low-spin iron(III) complex is a macrocycle¹⁵. In FeL_2^- , we have the first example of a complex incorporating an acyclic ligand.

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