

Magnetism and crystal structure of an N_3O_3 -coordinated iron(II) complex

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Received 22 April 2008

Accepted 6 May 2008

Online 21 May 2008

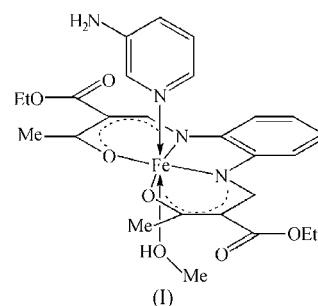
The reaction of $[FeL(MeOH)_2]$ [where L is the tetradentate N_2O_2 -coordinating Schiff base-like ligand (*E,E*)-diethyl 2,2'-[1,2-phenylenebis(nitrilomethylidyne)]bis(3-oxobutanoate)(2−) and MeOH is methanol] with 3-aminopyridine (3-apy) in methanol results in the formation of the octahedral complex (3-aminopyridine- κN^1){(*E,E*)-diethyl 2,2'-[1,2-phenylenebis(nitrilomethylidyne)]bis(3-oxobutanoate)(2−)- $\kappa^4 O^3, N, N', O^3$ }- (methanol- κO)iron(II), $[Fe(C_{20}H_{22}N_2O_6)(C_5H_6N_2)(CH_4O)]$ or $[FeL(3-apy)(MeOH)]$, in which the Fe^{II} ion is centered in an N_3O_3 coordination environment with two different axial ligands. This is the first example of an octahedral complex of this multidentate ligand type with two different axial ligands, and the title compound can be considered as a precursor for a new class of complexes with potential spin-crossover behavior. An infinite two-dimensional hydrogen-bond network is formed, involving the amine NH group, the methanol OH group and the carbonyl O atoms of the equatorial ligand. T -dependent susceptibility measurements revealed that the complex remains in the high-spin state over the entire temperature range investigated.

Comment

Octahedral iron(II) complexes are an interesting class of complexes because of the possible occurrence of the spin-crossover phenomenon. The ability to switch between two or more electronic states on the molecular level under changes in temperature, pressure or light is of potential interest for future applications in molecular switches or memory devices. Although spin crossover could be observed for any octahedral complex with a d^n ($n = 4-7$) electronic configuration, the spin transitions in octahedral iron(II) complexes with the diamagnetic low-spin (LS) and the paramagnetic high-spin (HS) states are by far the most thoroughly investigated. Of those iron(II) complexes that have been studied, about 90% exhibit N_6 coordination, while the others have N_4O_2 , N_4C_2 , $N_3C_2O_2$ or N_4S_2 coordination environments (Gütlich *et al.*, 1994; Goodwin, 1976; König, 1991; Kahn & Martinez, 1998).

So far, no examples with an N_3O_3 coordination environment are known.

In this paper, we present the structural and magnetic properties of the octahedral iron(II) complex (3-aminopyridine){(*E,E*)-diethyl 2,2'-[1,2-phenylenebis(nitrilomethylidyne)]bis(3-oxobutanoate)(2−)}(methanol)iron(II), (I), in which the Fe^{II} ion is centered in an N_3O_3 coordination environment. The complex was obtained in a one-pot reaction under argon by conversion of $[FeL(MeOH)_2]$ (L is the dibutanoate ligand) and 3-aminopyridine (3-apy) in methanol and heating to reflux for 1 h. A 30 molar excess of 3-apy was used in order to obtain a partial substitution of the axial methanol ligands and therefore an unsymmetric complex with two different axial ligands (Fig. 1).



The coordination around the Fe^{II} ion is almost ideal octahedral, with a displacement of the Fe^{II} ion from the N_2O_2 coordination plane towards the axial 3-apy ligand of about 0.08 Å. This is surprising, because with methanol as a relatively weak ligand in the axial position one could expect a larger distortion towards the stronger 3-apy ligand. Accordingly, the average bond lengths and angles within the first coordination sphere of the Fe^{II} center (Table 1) are within the range reported for similar octahedral iron(II) complexes with N_4O_2 coordination and the iron center in the high-spin state ($Fe-N_{eq} = 2.09$ Å and $Fe-O_{eq} = 2.04$ Å; Leibelng, 2003; Weber *et al.*, 2008). The equatorial $O2-Fe1-O1$ angle is a characteristic tool for the determination of the spin state of this type of iron(II) complex, because the angle changes from

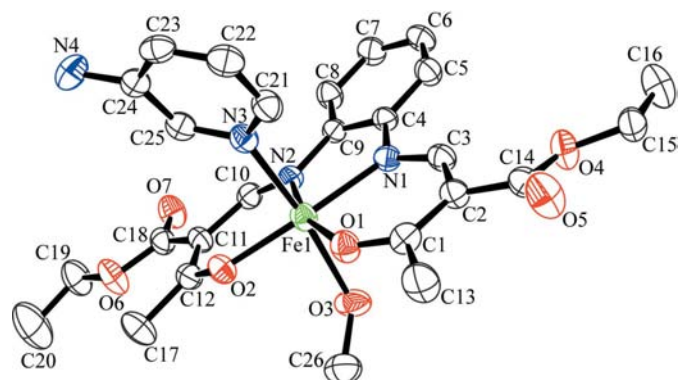


Figure 1
The molecular structure of (I), showing the atom labels and anisotropic displacement ellipsoids (drawn at the 50% probability level) for non-H atoms. H atoms have been omitted for clarity.

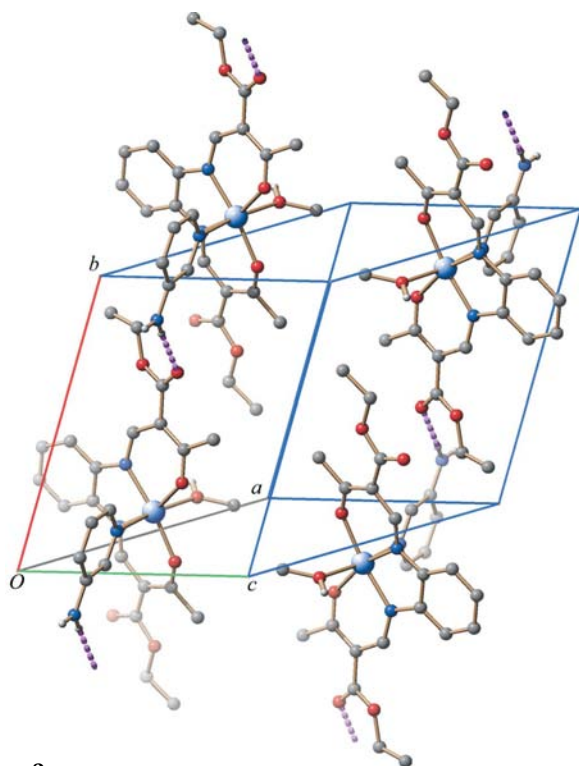


Figure 2
The molecular packing of (I), showing the N–H···O hydrogen bonds forming chains along [010]. C-bonded H atoms have been omitted for clarity.

about 110° in the HS state to about 90° in the LS state. At $110.64(6)^\circ$ in (I), this angle is in the region observed for N_4O_2 -coordinated iron(II) complexes in the HS state (Leibeling, 2003; Weber *et al.*, 2008). The heteroatoms of the axial ligands face one another almost linearly. A possible explanation for the minor distortion is the hydrogen-bond network in which the amine group of 3-apy is involved.

Intermolecular interactions such as hydrogen bonding, π stacking and van der Waals interactions are thought to play a central role for transmitting co-operative interactions during a spin transition in mononuclear complexes. In complex (I), three different hydrogen bonds (see Table 2) form an infinite two-dimensional network along the (101) plane. The base vectors are [010] and $[10\bar{1}]$. Amine atom N4 acts as a double hydrogen-bond donor, firstly *via* atom H4A to carbonyl atom O1ⁱ [symmetry code: (i) $-x, -y, -z + 1$], so that complexes with their axial 3-apy ligands directed towards one another are linked, and secondly *via* atom H4B to carboxylate atom O5ⁱⁱ [symmetry code: (ii) $x, y - 1, z$], linking the asymmetric units into chains along [010] (Fig. 2). The molecules are further linked by methanol atom O3, acting as a hydrogen-bond donor, *via* atom H31, to carboxylate atom O7ⁱⁱⁱ [symmetry code: (iii) $-x + 1, -y, -z$] of the equatorial ligand of a neighboring complex (Fig. 3). This interaction combined with the N4–H4A···O1ⁱ hydrogen bond links molecules in the $[10\bar{1}]$ direction.

At room temperature, the magnetic moment, expressed as the product $\chi_M T$, is $3.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is a typical value for iron(II) in the HS state. The moment remains almost

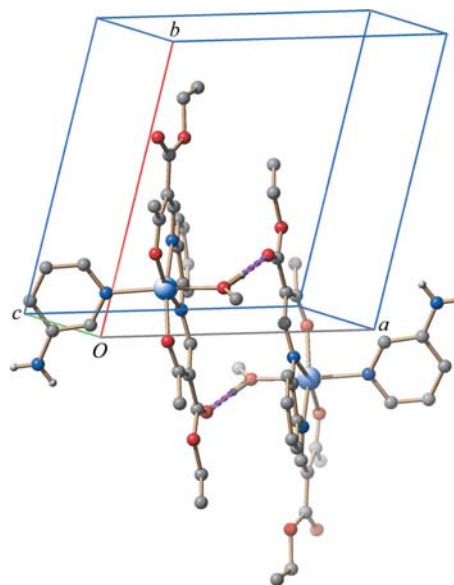


Figure 3
The molecular packing of (I), showing paired O–H···O hydrogen bonds linking inversion-related asymmetric units. C-bonded H atoms have been omitted for clarity.

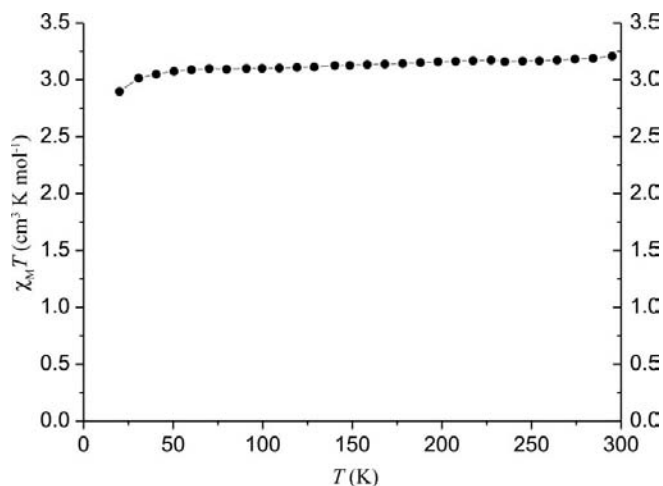


Figure 4
The thermal dependence of $\chi_M T$ for (I).

constant down to 25 K ($\chi_M T = 3.01 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$; Fig. 4), indicating that no spin crossover occurs. The decrease of $\chi_M T$ below 25 K is due to zero-field splitting. Obviously, the methanol ligand is too weak to put the overall ligand field in the spin-crossover region.

Experimental

The synthesis of (I) was carried out under argon using Schlenk tube techniques. $[\text{FeL}(\text{MeOH})_2]$ (Jäger *et al.*, 1985) and 30 equivalents of 3-aminopyridine (Fluka) were dissolved in absolute methanol (40 ml) and heated under reflux for 1 h. After 24 h, the product was filtered off and washed two times with ice-cold methanol. Pure crystals of (I) were obtained in a 70% yield. Analysis found: C 54.8, H 5.5, N 10.1%; $\text{C}_{26}\text{H}_{32}\text{FeN}_4\text{O}_7$ requires: C 54.9, H 5.7, N 9.9%. IR (PE): ν 3344 (*w*, NH), 1676 (*m*, COO), 1569 (*m*, CO) cm^{-1} . MS (DEI⁺, 70 eV): m/z (%) 442 (100) [M^+].

Crystal data

[Fe(C₂₀H₂₂N₂O₆)(C₅H₆N₂)(CH₄O)]
M_r = 568.40
 Triclinic, *P* $\bar{1}$
a = 11.234 (4) Å
b = 11.5760 (11) Å
c = 11.834 (3) Å
 α = 72.740 (17)°
 β = 75.67 (3)°
 γ = 68.91 (2)°
V = 1354.0 (6) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.61 mm⁻¹
T = 200 (2) K
 0.32 × 0.12 × 0.08 mm

Data collection

Oxford Xcalibur diffractometer
 23067 measured reflections
 4708 independent reflections
 2998 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.037

Refinement

R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.081
S = 0.94
 4708 reflections
 353 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max}$ = 0.34 e Å⁻³
 $\Delta\rho_{\min}$ = -0.21 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Fe1—O2	2.0298 (16)	Fe1—N2	2.0924 (18)
Fe1—O1	2.0489 (16)	Fe1—N3	2.2071 (19)
Fe1—N1	2.0896 (18)	Fe1—O3	2.2132 (19)
O2—Fe1—O1	110.64 (6)	N1—Fe1—N2	78.54 (7)
O2—Fe1—N1	163.09 (6)	O2—Fe1—O3	82.78 (7)
O1—Fe1—N2	163.46 (6)	N3—Fe1—O3	171.13 (7)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4A...O1 ⁱ	0.88	2.58	3.215 (3)	130
N4—H4B...O5 ⁱⁱ	0.88	2.20	3.068 (3)	171
O3—H31...O7 ⁱⁱⁱ	0.77 (3)	1.92 (3)	2.676 (3)	167 (4)

Symmetry codes: (i) -*x*, -*y*, -*z* + 1; (ii) *x*, *y* - 1, *z*; (iii) -*x* + 1, -*y*, -*z*.

Methanol atom H31 was refined isotropically. All other H atoms were located in difference maps and treated as riding on their parent atoms (N—H = 0.88 Å and C—H = 0.95–0.99 Å). One common *U*_{iso}(H) parameter for these H atoms was refined to 0.0649 (15) Å².

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *SCHAKAL99* (Keller, 1999); software used to prepare material for publication: *SHELXL97*.

The authors thank Sandra Albrecht for collecting the X-ray data and Moritz Reichvilser for his professional support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3144). Services for accessing these data are described at the back of the journal.

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