Revisited crystal symmetry of the high-spin form of the iron(II) spin-crossover complex dicyano[2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene]-iron(II) monohydrate

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The title iron(II) complex, $[Fe(CN)_2(C_{15}H_{23}N_3O_2)]\cdot H_2O$, is of interest to the spin-crossover community because of its unusual temperature-dependent magnetic behaviour as well as its relatively high relaxation temperature for the light-induced spin-crossover phenomenon. Structural modifications are strongly suspected to cause the unusual thermal spin-crossover features. Recently, the high-spin crystal structure has been reported but with an inadequate space group. In the present paper, the crystal structure is corrected by a new investigation, and some consequences for the structure–property relationships of this complex are discussed. The Fe^{II} ion is seven-coordinate and lies on a twofold axis.

Comment

Since its first description (Nelson *et al.*, 1986), the variable-temperature magnetic behaviour of the title spin-crossover compound, (I), has proved to be very unusual (König *et al.*, 1987; Hayami *et al.*, 2001) and is still debated. These properties will be detailed in a forthcoming paper (Sánchez Costa *et al.*, 2004). When cooling for the first time, this complex undergoes a sharp spin-crossover from a high-spin (HS) to a low-spin (LS) state at 160 K. Subsequent temperature changes strongly affect the features of the spin-crossover, such as the critical temperature, the hysteresis width and the relaxation process for the light-induced spin-crossover phenomenon. The commonly admitted justification to date for this difference between the first and a subsequent cooling has been that a major change of the molecular structure occurs at low temperature. It has been suggested that the Fe atom could undergo a modification from a six- to a seven-coordination sphere (König *et al.*, 1987). However, so far there is no experimental proof of this transition, which would be an unusual feature in the solid state.

(I)
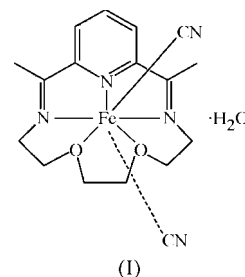
The crystal structure of this complex in its high-spin form has been determined at 250 K (Hayami *et al.*, 2001). The suggested unit-cell symmetry was monoclinic, *Cc*, and the determination revealed the presence of one solvent water molecule per iron complex. The water molecules and the complexes form infinite pseudo-chains along the *a* axis, and the Fe^{II} ion is in a pentagonal bipyramidal environment. Surprisingly, one of the two Fe—O bond lengths appears to be very long [2.405 (6) Å], while the other is in the expected range [2.277 (6) Å]. In addition, the structural data exhibit anomalies, such as, for instance, the high values of the shift/s.u. ratio after the final refinement cycle (0.386) and the unexplained value of the Flack parameter (−0.57; Flack, 1983). These anomalies could be due to a real physical phenomenon, such as, for example, a fraction of iron ions remaining in an LS state as a result of the relatively low temperature of the structural determination, or could simply reflect an error in the structural determination. On the basis of the available data, it was impossible to be sure of the nature of the problem raised by this structural report. In order to answer the question, we have recrystallized this complex and recollected the data at room temperature (293 K). The structure was solved and refined in the monoclinic *C2/c* space group without encountering any of the above problems. It is interesting to note that if the crystal structure is solved from our data set using the *Cc* space group then exactly the same anomalies as were present in the previous determination are obtained. Consequently, we assume that the true space group for the title complex is *C2/c*.
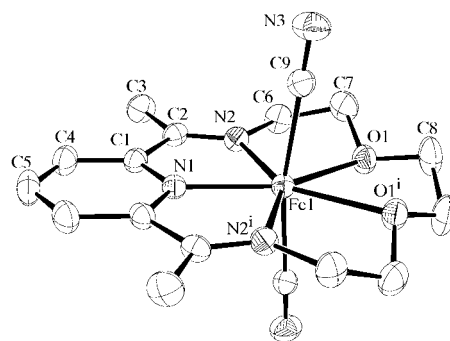

Figure 1
An *ORTEP*-3 (Farrugia, 1997) view of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme. The water molecules have been omitted for clarity. [Symmetry code: (i) $2 - x, y, \frac{1}{2} - z$.]

metal-organic compounds

The general description of the crystal packing is unchanged. However, the present space-group correction is of importance because it affects the iron environment. First, the iron coordination sphere angles (Table 1) are slightly different from the previously reported values; this difference could be crucial in the future when analysing the magnetic data. Indeed, the iron-environment distortion is known to influence the spin-crossover features strongly (Guionneau *et al.*, 2004). Furthermore, in the $C2/c$ unit cell, the iron ion lies on a twofold axis (Fig. 1), and so the two Fe—O bonds are crystallographically equivalent and of identical length (Table 1). The iron ion is thus unambiguously seven-coordinate at 293 K in the HS state. One consequence of importance is that, if there is a transition to a six-coordinate iron ion at low temperature, there must necessarily be a change in the crystal symmetry. Indeed, on going from an $FeN_3C_2O_2$ to an FeN_3C_2O coordination polyhedron, as expected, the two Fe—O bonds cannot remain symmetrically equivalent and the iron ion cannot lie on a twofold axis.

A large structural change at low temperature can also be predicted by consideration of the volume of the iron coordination sphere. The volume of the iron polyhedron has been widely studied for six-coordinate spin-crossover complexes (Guionneau *et al.*, 2002; Marchivie *et al.*, 2002; Thompson *et al.*, 2004). The calculation of this volume was performed from the atomic coordinates using *IVTON* (Balić Žunić & Vicković, 1996). It has been shown, on the basis of a large number of six-coordinate complexes, that the spin-crossover corresponds to a decrease of the polyhedron volume from 13.0 (5) (HS) to 10.0 (5) $Å^3$ (LS), *i.e.* a decrease of 25% (Guionneau *et al.*, 2004). Seven-coordinate spin-crossover iron complexes are very rare and such a statistical approach is not yet possible. For the title complex, the calculated volume of the iron polyhedron is 17.0 $Å^3$ in the HS state. Consequently, the expected transition from a seven-coordinate iron ion at room temperature (HS) to a six-coordinate iron ion at low temperature (LS) would correspond to a change of the iron polyhedron volume from 17.0 to 10.0 (5) $Å^3$. This large modification, almost 60% of the initial value, should be propagated to the whole molecular geometry and probably to the crystal packing.

The above remarks are consistent with the low-temperature single-crystal X-ray diffraction experiments that we have performed. Indeed, the single crystals are damaged when cooling, whatever the cooling rate. A large structural rearrangement is certainly the cause of this behaviour. Low-temperature single-crystal X-ray diffraction investigation being unsuccessful so far, a powder investigation should be attempted. We assume that the present results will then be useful in the analysis.

Experimental

The title complex was synthesized as described previously (Nelson *et al.*, 1986), except that the volume of the $[FeL(CN)_2]Cl_2$ solution was not reduced after the addition of NaCN. The entire solution was kept at a constant temperature of 293 K for a period of one week. The reaction yielded small prismatic dark-violet single crystals.

Crystal data

$[Fe(CN)_2(C_{15}H_{23}N_3O_2)]\cdot H_2O$	$D_x = 1.406$ Mg m^{-3}
$M_r = 401.25$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 6605
$a = 17.326$ (5) Å	reflections
$b = 12.054$ (5) Å	$\theta = 1.0$–27.5°
$c = 10.125$ (5) Å	$\mu = 0.82$ mm^{-1}
$\beta = 116.27$ (1)°	$T = 293$ (2) K
$V = 1896.2$ (13) Å^3	Prism, dark violet
$Z = 4$	$0.05 \times 0.05 \times 0.03$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.045$
ω scans with κ offsets	$\theta_{max} = 26.4°$
6183 measured reflections	$h = -21 \rightarrow 21$
1933 independent reflections	$k = -15 \rightarrow 15$
1590 reflections with $I > 2\sigma(I)$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$+ 1.1283P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.003$
1933 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
131 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H atoms: see below	

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	2.107 (2)	Fe1—N2	2.203 (2)
Fe1—C9	2.163 (3)	Fe1—O1	2.3342 (18)
N1—Fe1—C9	95.31 (6)	C9—Fe1—O1^i	83.65 (8)
C9—Fe1—C9^i	169.39 (12)	N2—Fe1—O1^i	142.69 (7)
N1—Fe1—N2	72.75 (5)	N1—Fe1—O1	144.40 (5)
C9—Fe1—N2	90.66 (9)	C9—Fe1—O1	87.72 (8)
C9^i—Fe1—N2	92.49 (9)	N2—Fe1—O1	71.76 (7)
N2—Fe1—N2^i	145.50 (10)	O1^i—Fe1—O1	71.20 (9)

Symmetry code: (i) $2 - x, y, \frac{1}{2} - z$.

All H atoms attached to C atoms were placed in calculated positions (C—H = 0.93–0.97 Å) and treated as riding. The H atoms of the water molecule, which lies in a general position and was assigned 0.5 occupancy, were located in a difference map and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) and *WinGX* (Farrugia, 1999); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX*.

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