Discontinuous High Spin ⇌ Low Spin Transition in an Iron(II) Complex [FeL₂(NCS)₂] with the Pharmaceutical Agent Bromazepam†

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A temperature-dependent susceptibility and Mössbauer effect study of the iron(II) complex [FeL₂(NCS)₂], where L is the psychotherapeutic agent bromazepam, has been performed. The Mössbauer spectra demonstrate that two lattice sites are present. One of them undergoes a high spin ($^5T_{2g}$) ⇌ low spin ($^1A_{1g}$) transition around ca. 240 K, the other remains in the low-spin state over the whole temperature range. This is consistent with the temperature dependence of the effective magnetic moment $\mu_{eff.}$, which varies between a pure low-spin value of 0.9 μ_B in the low-temperature region and an intermediate value of 4.2 μ_B as a high-temperature plateau. A small hysteresis for the high spin ⇌ low spin transition has been observed. It is suggested that two stereoisomers of [FeL₂(NCS)₂] with different magnetic properties are present in the lattice.

Bromazepam [7-bromo-1,3-dihydro-5-(2′-pyridyl)-2H-1,4-benzodiazepin-2-one, L] is a commercially available psychotherapeutic agent with bidentate α-di-imine ligand properties well suited for complex formation with transition-metal ions. Complexes of the types [ML₃]X₂·nH₂O (M = Fe^II; X = Cl, ClO₄, or SO₄) and [ML₂]X₂·nH₂O (M = Co, Ni, Cu, or Zn; X = Cl, ClO₄, or SO₄)[1,2] as well as the mixed-ligand complexes [ML₂(NCS)₂] (M = Co, Ni, Cu, or Fe^II)[3] have been synthesized and characterized with respect to their magnetic and spectral properties. For the complex [FeL₂(NCS)₂] an intermediate magnetic moment of 2.4 B.M. (at room temperature) was found,[3] and the authors suggested the existence of a high spin ⇌ low spin equilibrium, $^5T_{2g}(O_h)$ ⇌ $^1A_{1g}(O_h)$ in the approximation of O_h symmetry, in analogy to other iron(II) spin-crossover complexes of the class [Fe(ligand)₂(NCS)₂].[4]

The room-temperature magnetic moment of [FeL₂(NCS)₂] has also been found to depend considerably on the method of sample preparation. We have now performed a temperature-dependent magnetic susceptibility and Mössbauer effect study in order to explore the magnetism of [FeL₂(NCS)₂] more deeply. The sample used has a μ value of 4.2 at room temperature. A temperature-dependent high spin ⇌ low spin transition could indeed be established, but with a residual low-spin fraction at room temperature originating from the presence of an iron(II) species which remains low spin at all temperatures.

Experimental

Synthesis of [FeL₂(NCS)₂].—The method used in the present case differs from the earlier one.[3] A solution of bromazepam (9.48 × 10⁻⁴ mol) in methanol (40 cm³) was added to a solution of cis-[Fe(py)₄(NCS)₂] (py = pyridine) (4.74 × 10⁻⁴ mol) in methanol (30 cm³). The resulting deep purple precipitate was collected by filtration, washed several times with methanol, and dried in vacuum. The synthesis was carried out under an argon atmosphere. The purity of the compound was checked by elemental analysis (Found: C, 44.8; H, 2.50; N, 13.5; S, 6.95. Calc. for C₃₀H₂₀Br₂FeO₂S₂: C, 44.8; H, 2.50; N, 13.9; S, 6.95%).

Susceptibility Measurements.—Magnetic susceptibilities χ(T) were measured at temperatures between 140 and 320 K with

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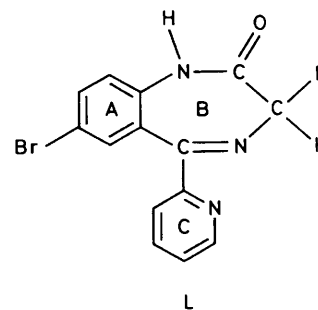
a Foner-type magnetometer equipped with a helium-flow cryostat in an external field of 1.8 T. The diamagnetic correction was calculated from Pascal constants (χ_{Dia} = −387 × 10⁻⁶ cm³ mol⁻¹).

Mössbauer Spectroscopy.—Mössbauer spectra between 150 and 300 K were recorded with a conventional Mössbauer spectrometer operating in the constant-acceleration mode. The source (⁵⁷Co/Rh) was kept at room temperature. The sample was placed in an Oxford flow cryostat. The statistics of the spectra suffers from the presence of bromine in the complex, which causes strong electronic absorption of the 14.4 keV radiation.

Results and Discussion

Figure 1 displays the effective magnetic moment $\mu_{eff.}$ as a function of temperature. Below 180 K, $\mu_{eff.}(T)$ merges into a constant plateau at ca. 0.9 indicating that the compound has reached quantitatively the low-spin state. The $\mu_{eff.}$ value of 0.9 is typical for this class of complexes,[4] but does not appear to arise from a residual fraction of high-spin molecules in the present case as concluded from the Mössbauer spectra. Between 200 and 260 K, $\mu_{eff.}$ increases reflecting the low spin to high spin conversion. The spin transition is rather discontinuous and occurs mainly in the range between 220 and 250 K. A detailed inspection of the data reveals that the transition curve shows a small hysteresis with a width of ca. 2 K. Above 260 K the spin transition is nearly complete and $\mu_{eff.}$ remains constant at 4.2, which is well below the value expected for a pure high-spin

Table. Mössbauer parameters (mm s^{-1}) for [FeL$_2$(NCS)$_2$]. The spectra were collected in the heating mode

	Low spin (A)		Low spin (B)		High spin		Area fraction		
T/K	ΔE_Q	δ	ΔE_Q	δ	ΔE_Q	δ	ls(A)	ls(B)	hs
150	0.41(2)	0.23(1)	0.70(1)	0.28(1)	—	—	0.25(3)	0.75(3)	—
200	0.43(2)	0.22(1)	0.69(1)	0.26(1)	—	—	0.25(3)	0.75(3)	—
220	0.42(2)	0.21(1)	0.69(1)	0.26(1)	—	—	0.24(2)	0.76(2)	—
240	0.42^a	0.19(1)	0.69^a	0.24(1)	2.95(2)	0.86(1)	0.25(2)	0.51(2)	0.24(1)
250	0.42^a	0.15(1)	0.69^a	0.16(2)	2.93(1)	0.86(1)	0.26(2)	0.16(2)	0.60(1)
260	0.42^a	0.13(1)	0.69^a	0.13(2)	2.90(1)	0.86(1)	0.24(2)	0.13(2)	0.63(1)
270	0.42^a	0.13(1)	0.69^a	0.12(3)	2.86(1)	0.86(1)	0.22(2)	0.12(2)	0.67(1)
300^b	0.51(3)	0.12(2)	—	—	2.72(1)	0.83(1)	0.27(2)	—	0.73(2)

^{a} Parameter not varied. ^{b} The spectrum was fitted with one low-spin quadrupole doublet.
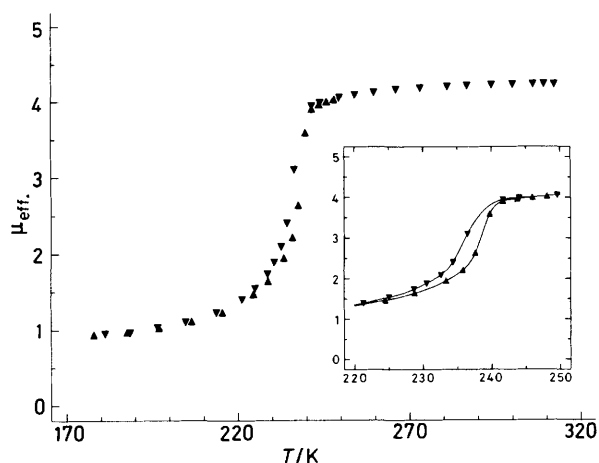


Figure 1. Plot of effective magnetic moment $\mu_{eff.}$ vs. temperature for [FeL$_2$(NCS)$_2$]

complex of iron(II), 4.9 (spin only). The residual fraction of molecules which is still in the low-spin state may be estimated using the expression (1) where hs and ls denote the pure high-

$$(\mu_{eff.})^2 = \gamma_{ls}(\mu_{eff.}^{ls})^2 + (1 - \gamma_{ls})(\mu_{eff.}^{hs})^2 \qquad (1)$$

spin and low-spin phases, respectively, and γ_{ls} is the low-spin fraction. Assuming a spin-only moment for the high-spin state of $\mu_{eff.}^{hs} = 4.9$ and taking the low-temperature value of 0.9 for $\mu_{eff.}^{ls}$ we obtain $\gamma_{ls} = 0.27$ as a lower limit for the low-spin fraction near room temperature.

The Mössbauer spectra of [FeL$_2$(NCS)$_2$] recorded between 150 and 300 K are shown in Figure 2. Those at 150 and 200 K consist of an asymmetric doublet with a shoulder in the high-velocity component. The spectra were fitted to four Lorentzians, corresponding to two doublets [denoted as ls(A), ls(B) in Figure 2]. The isomer shifts and quadrupole splittings are characteristic for iron(II) in the low-spin state (cf. Table). From the area ratios of the two resonance doublets we find the fractions of 0.25 for species ls(A) and 0.75 for species ls(B). At 240 K, a third doublet (denoted as hs in Figure 2) with a large quadrupole splitting and an isomer shift characteristic for iron(II) in the high-spin state appears. At the same time the outer low-spin doublet ls(B) loses intensity. At ca. 250 K the high-spin resonances are dominant. The spectra recorded at 240, 250, and 260 K were evaluated with six Lorentzians corresponding to three doublets, where the quadrupole splittings of the low-spin doublets were assumed to be temperature independent. Above
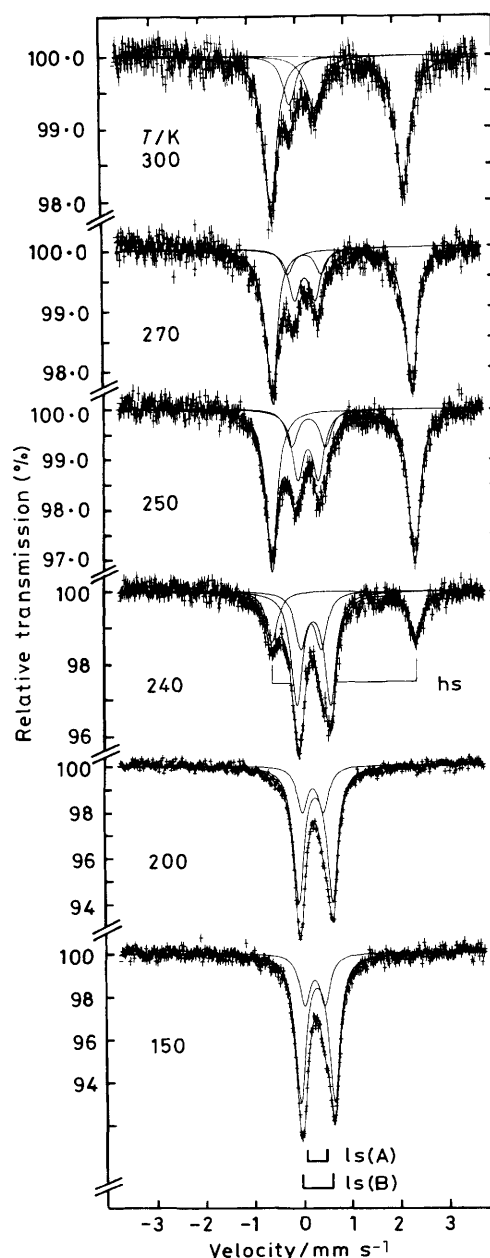
Figure 2. Iron-57 Mössbauer spectra of [FeL$_2$(NCS)$_2$]

260 K only minor changes in the spectra are observed. Evaluating the spectrum at 300 K with two doublets, one for the high-spin and one for the low-spin state, yields a quadrupole splitting of 0.51 mm s^{-1} for the low-spin doublet and a residual low-spin fraction of 0.27 (see Table). Both values are similar to those of doublet ls(A) in the low-temperature spectra. We may, therefore, conclude that two kinds of complex molecules coexist in the lattice. One of them undergoes a discontinuous high spin $\rightleftharpoons$ low spin transition with a small hysteresis, the other remains in the low-spin state over the whole temperature range studied. The results derived from the Mössbauer spectra compare well with those from the susceptibility study where a low-spin fraction of 0.27 was estimated as a lower limit.

These results do not support the polymeric structure suggested previously for the [FeL$_2$(NCS)$_2$] complex[3] where the two bromazepam ligands are believed to form an equatorial plane and the two NCS groups are located in axial positions, one N-bonded and the other S-bonded to the iron centre. Most spin-crossover complexes of iron(II) are known to have a FeN$_6$ core.[4] If one of the NCS groups were co-ordinated via the S atom as suggested for the polymeric structure, the ligand-field strength would most probably be decreased to such an extent that it becomes smaller than the mean spin-pairing energy and a pure high-spin complex would be anticipated. An iron(II) spin-crossover complex with a FeN$_5$S core is not known. Rather we believe that the Mössbauer spectra and the magnetic behaviour of [FeL$_2$(NCS)$_2$] can be rationalized by the presence of two different stereoisomers of the complex with the NCS groups in cis positions of the octahedron, but both co-ordinated via the N atoms. This arrangement would be similar to that in [Fe(bipy)$_2$(NCS)$_2$] (bipy = 2,2'-bipyridine)[5] and could be inferred from the method of synthesis employed in the present study, where the ligand L was added to cis-[Fe(py)$_4$(NCS)$_2$] for subsequent stepwise pyridine substitution. As the two N atoms of the bidentate ligand L are not equivalent, three geometrical isomers of the iron complex are possible as shown below where

	(I)	(II)	(III)
N(py)/N(py)	cis	cis	trans
N(im)/N(im)	trans	cis	cis

N(py) are the pyridine N atoms and N(im) the imine N atoms of L. A similar example of stereoisomers with different magnetic properties has been reported for tris(2-aminomethylpyridine)-iron(II) iodide.[6] A crystal structure determination revealed that in the lattice of this compound the mer isomer of the cation with iron(II) in the high-spin state coexists with the fac isomer exhibiting a high spin $\rightleftharpoons$ low spin equilibrium near room temperature.

The lower magnetic moment for [FeL$_2$(NCS)$_2$] at room temperature found in the previous study[3] indicates that a lower amount of the isomer showing a high spin $\rightleftharpoons$ low spin transition was formed by the synthetic method employed.

It would be desirable to check these conclusions by an X-ray structure determination of [FeL$_2$(NCS)$_2$]. Unfortunately, so far it has not been possible to obtain suitable single crystals of the compound.

Acknowledgements

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