

# MÖSSBAUER AND MAGNETIC STUDIES OF COPPER(II)- PHTHALOCYANINE EFFECT ON THE SPIN STATES OF BIS(*N*-*o*-TOLYL-2-IMIDAZOLALDIMINE)IRON(II) DITHIOCYANATE

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**Abstract**—The mononuclear complex of general formula  $[\text{Fe}^{\text{II}}(\text{TIA})_2(\text{NCS})_2]$  (**1**) and the heterotrinnuclear complex of  $(\text{Cu}-\text{Pc})_2[\text{Fe}(\text{TIA})_2(\text{NCS})_2]$  (**2**), where TIA = *N*-*o*-tolyl-2-imidazolaldimine and Pc = phthalocyanine, have been synthesized. The X-ray crystal structure of **1** shows it to consist of two NCS groups in the *cis* position. The magnetic properties of the complexes have been measured down to 4.2 K and Mössbauer spectra have been recorded down to 20 K. In **1**, the iron(II) is pure high-spin  $S = 2$  ( $^5T_2$ ) over the whole temperature range. In **2**, a gradual spin crossover ( $^5T_2 \leftrightarrow ^1A_1$ ) occurs below 298 K and the spin crossover is incomplete since it still presents a high-spin fraction about 0.35, even at 4.0 K.

The spin transition between high-spin and low-spin ground states in iron complexes have continued to be of interest because of the biological relevance of the spin-crossover phenomenon<sup>1,2</sup> and the fundamental issues of what factors control the spin-state or the spin-crossover in the solid state of iron compounds.<sup>3-7</sup>

Recently, we have found that the spin state of iron(III) in the model complexes of cytochrome *c* oxidase such as  $\text{X}_2\text{Fe}_2(\text{TPP})_2(\text{Apen})\text{Cu}_2\text{Cl}_4$ , where X is an axial ligand of FeTPP, TPP = 5,10,15,20-tetraphenylporphine and Apen = bis(acetylpyrazine)ethylenediimine, was controlled by changing the X group and the bridged secondary metal complex (Apen) $\text{Cu}_2\text{Cl}_4$  moiety.<sup>8,9</sup> As X = imidazolate, the thermally induced spin-crossover of  $^6A_1 \leftrightarrow ^2T_2$  of iron(III) in the complex was observed.<sup>9</sup>

However, it is well known that the imidazole-bonded mononuclear  $(\text{Im})_2\text{Fe}(\text{TPP})$  contains the temperature-independent low-spin state of  $\text{Fe}^{\text{III}}$ .<sup>10</sup> Recently, the effect of secondary metal complex on the spin state in the iron(III) complex also has been observed.<sup>11,12</sup> The spin-state transition has become of renewed interest because of the potential offered by the secondary metal complex effect on the spin-state transition for the understanding of the factors of the effect on the spin-state variety in the metalloenzymes.<sup>13</sup>

In this paper, we report the preparation and variable-temperature magnetic and Mössbauer spectroscopic studies on the spin state of iron(II) in  $\text{FeL}_2(\text{NCS})_2$  (**1**) and  $[\text{Cu}^{\text{II}}-\text{Pc}]_2\text{FeL}_2(\text{NCS})_2$  (**2**), where L = *N*-*o*-tolyl-imidazolaldimine (TIA) (see Fig. 1), Pc = phthalocyanine. The purpose of this work was to specify the role of the macrocyclic copper(II) complex on changing the spin state of the iron(II) atom in the present heterotrinnuclear

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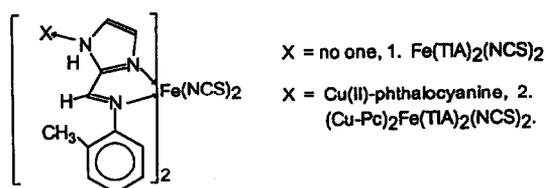


Fig. 1. The proposed molecular structures of the complexes.

$\text{Cu}_2^{\text{II}}\text{-Fe}^{\text{II}}$  complex. Moreover, a detailed single-crystal X-ray diffraction structural analysis of the new complex of  $\text{Fe(TIA)}_2(\text{NCS})_2$  is also reported.

## EXPERIMENTAL

### Preparation of *N*-*o*-tolyl-2-imidazolaldimine (TIA)

2-Imidazolecarboxaldehyde (0.96 g, 10 mmol) was added to 50 cm<sup>3</sup> hot alcohol. *o*-Toluidine (0.93 g, 10 mmol) was then added, the mixture was stirred for 1 h, after evaporating the solvent, and a white powdery solid was obtained. Recrystallization from methanol gave white needles. Found: C, 71.1; H, 5.5; N, 22.4. Calc. for  $\text{C}_{11}\text{H}_{11}\text{N}_3$ : C, 71.3; N, 6.0; H, 22.7%. M.p. = 149°C. <sup>1</sup>H NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  2.3 (s,  $\text{CH}_3$ ), 6.8–6.9 (m, imidazole 2H), 7.0–7.2 (m, 4H of benzene ring), 8.2 (s, 1 H), 11.8 (s, H—N of imidazole ring). IR ( $\text{cm}^{-1}$ , KBr): 1640 (CN str. of aldimine).

### Preparation of complexes

All preparations were carried out under nitrogen using air-free water and ethanol. All compounds were dried *in vacuo* over silica gel at room temperature.

$\text{Fe(TIA)}_2(\text{NCS})_2$  (**1**). To a solution of TIA (0.37 g, 2 mmol) in hot ethanol (20 cm<sup>3</sup>) was added a fresh aqueous solution of  $\text{FeSO}_4$  (0.278 g, 1 mmol). The mixture was stirred, then an aqueous solution of  $\text{NH}_4\text{NCS}$  (0.152 g, 2 mmol) added. The reddish brown crystals which formed were filtered off, washed with ethanol and dried *in vacuo* over  $\text{P}_2\text{O}_5$ . Crystals of compound **1** for X-ray crystal analysis were grown by keeping in concentrated ethanol at 20°C overnight under a nitrogen atmosphere in a dry box. Found: C, 53.1; H, 4.1; N, 20.3. Calc. for  $\text{C}_{24}\text{H}_{22}\text{FeN}_8\text{S}_2$ : C, 53.1; H, 4.1; N, 20.7%. M.p. = 251°C. IR ( $\text{cm}^{-1}$ , KBr): 2078, 2068 (CN str. of NCS) and 1620 (CN str. of aldimine).

$(\text{Cu-Pc})_2\text{Fe(TIA)}_2(\text{NCS})_2$  (**2**). To a solution of **1** (0.566 g, 1 mmol) in dichloromethane was added a solution of copper(II)-phthalocyanine (Cu-Pc; 1.15 g, 2 mmol) in petroleum ether. This solution was stirred for 1 h and set aside to stand overnight

under nitrogen in a dry box. The black crystals which formed were filtered off and dried *in vacuo*, yield 65%. Found: C, 62.7; H, 3.42; N, 20.1.  $(\text{Cu-Pc})_2\text{Fe(TIA)}_2(\text{NCS})_2$  requires: C, 62.4; H, 3.2; N, 19.8%. M.p.: over 300 K. IR ( $\text{cm}^{-1}$ , KBr): 2080, 2068 (CN str. of NCS) and 1630 (CN str. of aldimine).

### X-ray structure determination

Crystallographic data for **1** are given in Table 1. X-ray data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo- $K_\alpha$  radiation. Total number of reflections 2265 [ $1744 > 2.0 \sigma(I)$ ] were measured up to  $2\theta$  of 50° in the = *h*, +*k*, +*l* octants. The structure was solved by the heavy atom method and subsequent difference Fourier maps followed by full-matrix least-squares refinement. Selected bond lengths and bond angles appear in Table 2. Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters and structure factor tables are included as supplementary material.

### Spectra

IR spectra in the range 4000–400  $\text{cm}^{-1}$  were obtained on a Shimadzu IR-470 or a Bio-rod model FTS-40 FT IR spectrophotometer. <sup>1</sup>H NMR spectra of the ligand were recorded on Bruker WP-100SY and WH300 instruments using tetramethylsilane as internal standard. <sup>57</sup>Fe Mössbauer spectra in the temperature range 298–20 K were obtained on an Austin S-600 Mössbauer spectrometer of constant acceleration; <sup>57</sup>Co(Pd) was used as the radiation source. Iron foil was used as the standard for the isomer shift.

### Magnetic measurements

Magnetic susceptibilities  $\chi_m(T)$  of the powder samples were measured between 4 and 300 K at a field of 10 kG using a Quantum Design Model MPMS SUID magnetometer. Diamagnetic corrections were made using Pascal's constant.<sup>14</sup> The magnetic moment,  $\mu_{\text{eff}}$ , was obtained from the relationship  $\mu = 2.828 (\chi_m T)^{1/2}$ .

## RESULTS AND DISCUSSION

### Description of the structure

The coordination geometry about iron and the atom numbering scheme in  $\text{Fe(TIA)}_2(\text{NCS})_2$  (**1**) are shown in Fig. 2. Coordination number 6 for each

Table 1. Crystallographic data for Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub>

Formula	FeS <sub>2</sub> C <sub>24</sub> N <sub>8</sub> H <sub>22</sub>
Formula weight	542.45
Diffractometer used	CAD4
Space group	C2/c
<i>a</i> (Å)	9.710(2)
<i>b</i> (Å)	16.121(2)
<i>c</i> (Å)	16.438(3)
β (°)	91.07(2)
<i>V</i> (Å <sup>3</sup> )	2572.6(8)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.401
λ(Mo-K <sub>α</sub> ) (Å)	0.71069
<i>F</i> (000)	1120
Unit cell detection; no.; 2θ range	24, (18.61–24.55)
Scan type	θ–2θ
2θ scan width (°)	2(0.9+0.35 tan θ)
2θ range (°)	50
μ(Mo-K <sub>α</sub> ) (cm <sup>-1</sup> )	7.7
Crystal size (mm)	0.5 × 0.5 × 0.6
Temperature (K)	298
No. of unique reflections	2265
No. of obs. reflections [ <i>I</i> > 2σ( <i>I</i> )]	1744
No. of refined parameters	160
<i>R</i> , <i>R</i> <sub>w</sub>	0.044; 0.040
GoF	2.79
Minimized function	Σw  <i>F</i> <sub>0</sub> – <i>F</i> <sub>c</sub>   <sup>2</sup>
Weighting scheme	1/[σ <sup>2</sup> ( <i>F</i> <sub>0</sub> ) + 0.00001 <i>F</i> <sub>0</sub> <sup>2</sup> ]
<i>g</i> (second. ext. coeff.) × 10 <sup>4</sup>	0.26(9)
(Δ/σ) <sub>max</sub>	0.053
(Δρ) <sub>min,max</sub> (e Å <sup>-3</sup> )	–0.37, 0.40
Computation program	NRCVAX <sub>b</sub>

<sup>a</sup>*R* = [Σ|*F*<sub>0</sub>–*F*<sub>c</sub>|/*F*<sub>0</sub>]. *R*<sub>w</sub> = [Σ w(|*F*<sub>0</sub>–*F*<sub>c</sub>|<sup>2</sup>/Σ w(|*F*<sub>0</sub>|<sup>2</sup>)]<sup>1/2</sup>; σ<sup>2</sup>(*F*<sub>0</sub>) from counting statistics.

<sup>b</sup>NRCVAX: E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.* 1989, **22**, 384.

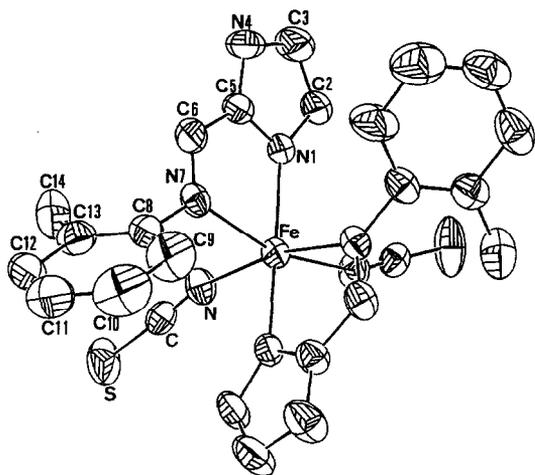


Fig. 2. ORTEP stereoview of Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub> (**1**) with hydrogen atoms omitted (50% probability thermal ellipsoids).

iron(II) is completed by six nitrogen atoms belonging to two TIA and two thiocyanate groups in *cis* positions. The Fe–N bond lengths involving NCS [Fe–N = 2.096(3) Å] are shorter than those involving the *N*-imidazole moiety [Fe–N(1) = 2.133(3) Å] and *N*-aldimine moiety [Fe–N(7) = 2.318(3) Å], which leads to a pronounced rhombic distortion of the FeN<sub>6</sub> octahedron. Furthermore, whereas the N–C–S groups are quasi-linear, the Fe–N–C(S) linkages are significantly bent [Fe–N–C = 160.7(3)°]. These main structural parameters of **1** are found to be the limit to the homologous values reported for the spin-crossover complexes Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>,<sup>15</sup> Fe(bpy)<sub>2</sub>(NCS)<sub>2</sub>,<sup>16</sup> Fe(btz)<sub>2</sub>(NCS)<sub>2</sub> (btz = 2,2'-bis-4,5-dihydrothiazine)<sup>17</sup> and [(Fe)bpym(NCS)<sub>2</sub>]·2bpym (bpym = 2,2'-bipyrimidine).<sup>18</sup> In these compounds, the average distances of Fe–CN(heterocycle) bonds range from 2.17 to 2.22 Å, and

those for Fe—N—(CS) bonds vary from 2.05 to 2.09 Å.

The most notable IR spectra of the ligand TIA and the complexes **1** and **2** are characteristics of CN stretching absorptions in the aldimine moiety (Im-HC = *N*-*o*-totyl) and NCS<sup>-</sup> groups. In the spectrum of the free ligand TIA,  $\nu$  (CN str of aldimine) at 1640 cm<sup>-1</sup> is shifted to 1620 and 1630 cm<sup>-1</sup> due to chelation with the iron atom in complexes **1** and **2**, respectively. The thiocyanate group exhibits a fundamental C—N(S) stretching frequency which depends on whether the group is bonded to the metal ion through nitrogen or sulphur, respectively. For nitrogen-bonded thiocyanate, the absorption range is proposed at 2040–2080 cm<sup>-1</sup>.<sup>19</sup> The IR spectra at 298 K for **1** and **2** show two sets absorption bands at 2078, 2068 and 2080, 2068 cm<sup>-1</sup>, respectively. It can be inferred that the two IR modes of these bands are the symmetric and asym-

metric nitrogen-bonded CN stretches, both of which are expected to be IR active in a distorted *cis* octahedral ligand field symmetry.<sup>20</sup> Clearly, these results are consistent with those observed in the crystallographic study of **1**.

#### Magnetic susceptibility data

The results of magnetic measurements on Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub> (**1**) and (Cu—Pc)<sub>2</sub>Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub> (**2**) in the temperature range between 4 and 300 K are plotted in Fig. 3. The temperature limit for the moment of **1** is 4.90 ± 0.05 at 300 K. With decreasing temperature, i.e. down to 20 K, the moment closely follows the theory of paramagnetism for the distorted octahedral high-spin Fe<sup>II</sup> (*S* = 2) state. The magnetic moment of **2** as shown in Fig. 3 decreases gradually from 4.65 at 300 K to 2.88 at 4.0 K. The value of the magnetic moment (4.65 at

Table 2. Selected bond distances (Å) and angles (°) for Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub>

Fe—N	2.096(3)	N(4)—C(5)	1.340(5)
Fe—Na	2.096(3)	C(5)—C(6)	1.444(5)
Fe—N(1)	2.133(3)	C(6)—N(7)	1.270(5)
Fe—N(1) <sup>a</sup>	2.133(3)	N(7)—C(8)	1.434(4)
Fe—N(7)	2.318(3)	C(8)—C(9)	1.411(6)
Fe—N(7) <sup>a</sup>	2.318(3)	C(8)—C(13)	1.374(5)
N—C	1.148(4)	C(9)—C(10)	1.370(6)
C—S	1.635(4)	C(10)—C(11)	1.367(7)
N(1)—C(2)	1.365(4)	C(11)—C(12)	1.361(6)
N(1)—C(5)	1.319(4)	C(12)—C(13)	1.434(6)
C(2)—C(3)	1.349(5)	C(13)—C(14)	1.444(6)
C(3)—N(4)	1.354(5)		
N—Fe—N <sup>a</sup>	98.11(12)	N(1)—C(2)—C(3)	109.6(3)
N—Fe—N(1)	102.63(11)	C(2)—C(3)—N(4)	106.4(3)
N—Fe—N(1) <sup>a</sup>	88.95(11)	C(3)—N(4)—C(5)	107.5(3)
N—Fe—N(7)	88.62(10)	N(1)—C(5)—N(4)	110.9(3)
N—Fe—N(7) <sup>a</sup>	163.54(11)	N(1)—C(5)—C(6)	121.2(3)
Na—Fe—N(1)	88.95(11)	N(4)—C(5)—C(6)	127.9(3)
Na—Fe—N(1) <sup>a</sup>	102.63(11)	C(5)—C(6)—N(7)	117.2(3)
Na—Fe—N(7)	163.54(11)	Fe—N(7)—C(6)	112.07(22)
Na—Fe—N(7) <sup>a</sup>	88.62(10)	Fe—N(7)—C(8)	129.16(21)
N(1)—Fe—N(1) <sup>a</sup>	162.41(11)	C(6)—N(7)—C(8)	118.6(3)
N(1)—Fe—N(7)	74.89(10)	N(7)—C(8)—C(9)	116.7(3)
N(1)—Fe—N(7) <sup>a</sup>	92.44(10)	N(7)—C(8)—C(13)	120.8(3)
N(1) <sub>a</sub> —Fe—N(7)	92.44(10)	C(9)—C(8)—C(13)	122.5(3)
N(1) <sub>a</sub> —Fe—N(7) <sup>a</sup>	74.89(10)	C(8)—C(9)—C(10)	118.2(4)
N(7)—Fe—N(7) <sup>a</sup>	88.98(10)	C(9)—C(10)—C(11)	119.8(4)
Fe—N—C	160.7(3)	C(10)—C(11)—C(12)	123.4(4)
N—C—S	178.8(3)	C(11)—C(12)—C(13)	118.4(4)
Fe—N(1)—C(2)	139.99(23)	C(8)—C(13)—C(12)	117.6(4)
Fe—N(1)—C(5)	114.42(22)	C(8)—C(13)—C(14)	123.0(3)
C(2)—N(1)—C(5)	105.6 (3)	C(12)—C(13)—C(14)	119.4(4)

<sup>a</sup>(1 - *x*, *y*, 0.5 - *z*).

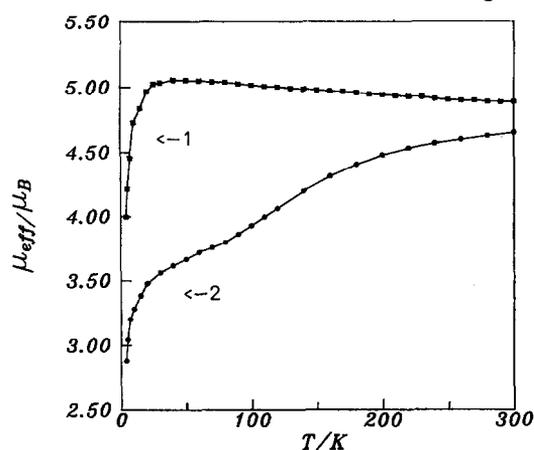


Fig. 3. Temperature dependence of magnetic moments for Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub> (1) and (Cu-Pc)<sub>2</sub>Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub> (2).

300 K) is lower than that calculated for a totally non-coupled spin-only high-spin Fe<sup>II</sup> ( $S = 2$ ,  ${}^5T_2$ ) and 2Cu<sup>II</sup> ( $S = 1/2$ ) system,  $\mu_{\text{eff}} = (4.90^2 + 2 \times 1.73^2)^{1/2} = 5.48$ ; this implies that there is antiferromagnetic spin-exchange between two Fe<sup>II</sup>-Cu<sup>II</sup> atoms or that there is a spin transition (between high-spin and low-spin) in (Cu-Pc)<sub>2</sub>Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub>. The magnetic moment of 2 decreases gradually from 4.65 at 300 K to 2.88 at 4.0 K. Clearly these values include the behaviours of an antiferromagnetic spin coupling between high-spin Fe<sup>II</sup> ( $S = 2$ ) and Cu<sup>II</sup> ( $S = 1/2$ ) atoms and a spin-crossover of the Fe<sup>II</sup> in this complex. Furthermore, the value of the magnetic moment at 4.0 K of 2 is 2.88, which is greater than that calculated for a totally non-coupled spin-only of low-spin Fe<sup>II</sup> ( $S = 0$ )-Cu<sup>II</sup> ( $S = 1/2$ ) system. This implies that the spin transition from  ${}^5T_2$  to  ${}^1A_1$  of Fe<sup>II</sup> in the complex is incomplete, even at 4.0 K.

#### Mössbauer spectra

Figures 4 and 5 show a selection of some representative  ${}^{57}\text{Fe}$  Mössbauer spectra obtained at decreasing temperatures for 1 and 2, respectively. The temperature-dependent Mössbauer spectra of 1 (298–78 K) show only one quadrupole doublet with I.S. = 0.87 (300 K)–1.06 mm s<sup>-1</sup> (78 K) and Q.S. = 2.69 (300 K)–2.92 mm s<sup>-1</sup> (78 K), which corresponds to the  $S = 2$  high-spin ground state of iron(II). Additional support for the assignment is provided by the magnetic data as described above. The variable-temperature zero-field Mössbauer spectra of 2 (as shown in Fig. 5) show the high-spin ( ${}^5T_2$ )  $\leftrightarrow$  low-spin ( ${}^1A_1$ ) transition of iron(II). The

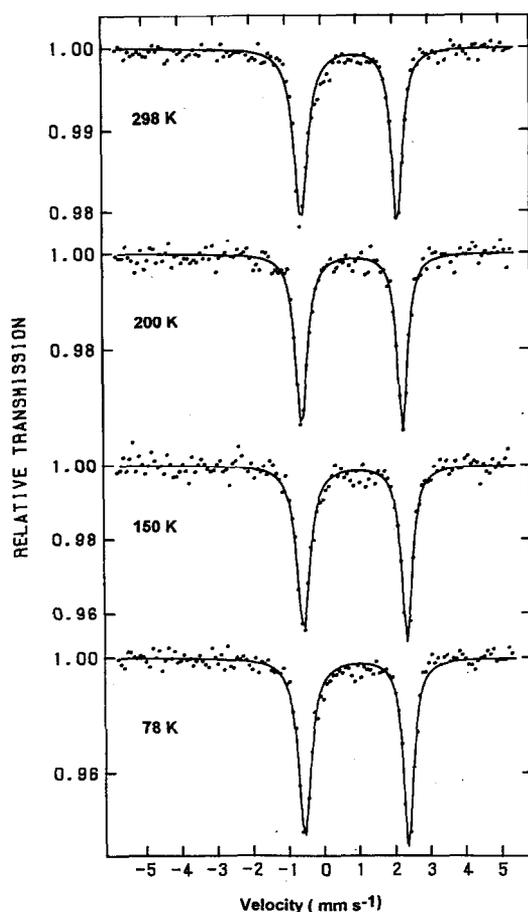


Fig. 4.  ${}^{57}\text{Fe}$  Mössbauer spectra of Fe(TIA)<sub>2</sub>(NCS)<sub>2</sub>.

dominant quadrupole asymmetric doublet absorption with I.S. = 0.75 and Q.S. = 2.38 mm s<sup>-1</sup> observed at 298 K is characteristic of a  ${}^5T_2$  ground state.

Asymmetric absorption is due to overlapping of a portion of low-spin species of iron(II) with lower I.S. and Q.S. Additional support for the assignment is provided by the magnetic data; e.g. 4.64  $\mu_B$  at 298 K. As the temperature is lowered, another quadrupole doublet appears (between the two previous peaks), the intensity of which increases at the expense of that of the first one. On the basis of the I.S. = 0.25 and Q.S. = 0.68 mm s<sup>-1</sup> data at 20 K, the new doublet may be assigned to the  $S = 0$  ( ${}^1A_1$ ) low-spin ground state of iron(II). The assignment is consistent with the decrease of the magnetic moment to 3.6 at 20 K. From the area ratio of the Mössbauer spectra, if the Debye–Waller factor (recoilless fraction) of  $f({}^5T_2)$  and  $f({}^1A_1)$  is the same here, the fraction of the sample present in the low-spin form at 20 K is 0.65, thus indicating that the spin crossover is incomplete, even at 20 K, with about 35% high-spin  ${}^5T_2$  ground state of iron(II) in the complex. These results clearly indicate that

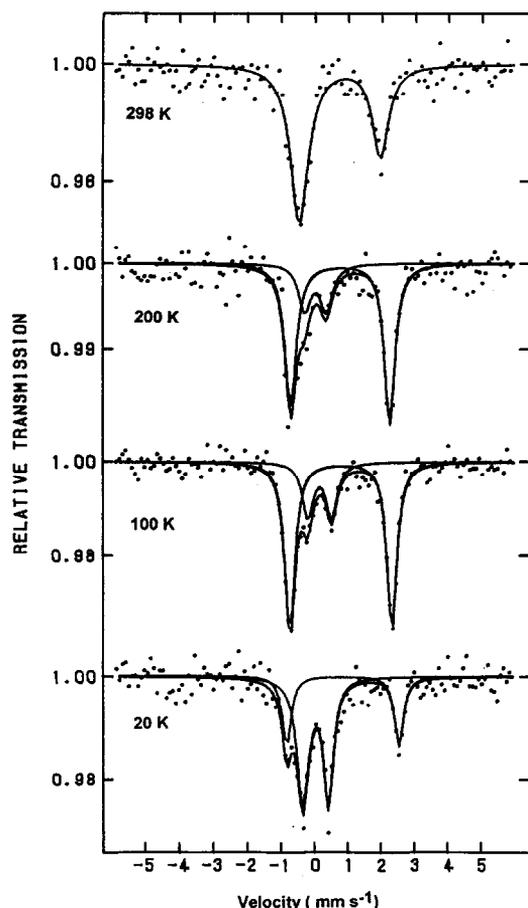


Fig. 5.  $^{57}\text{Fe}$  Mössbauer spectra of  $(\text{Cu-Pc})_2\text{Fe}(\text{TIA})_2(\text{NCS})_2$ .

the thermal spin crossover behaviour occurring in  $(\text{Cu}^{\text{II}}\text{Pc})_2\text{Fe}(\text{TIA})_2(\text{NCS})_2$  is affected by the secondary metal complex  $\text{Cu}^{\text{II}}\text{-Pc}$  on the field strength of the TIA ligand. Thus, the field strength is appropriate to produce a spin crossover situation for iron(II).

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