Synthesis and Mössbauer effect studies of low dimensional organoiron compound Fe(py)$_3$Cl$_3$·py

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Abstract

The Fe(py)$_3$Cl$_3$·py complexes (where py is the pyridine molecule) of iron(III) have been prepared by the reaction of anhydrous ferric chloride with pyridine. Crystals of Fe(py)$_3$Cl$_3$·py may occur in two crystallographic systems: orthorhombic and monoclinic with the structural phase transition at a temperature close to 200 K. The obtained Mössbauer parameters of these complexes provide the possibility to determine the pyridine stoichiometry, electron spin and oxidation states of iron in single crystals.

Introduction

Organometallic compounds, including transition elements, due to a wide variety of interatomic and intermolecular interactions exhibit interesting highly anisotropic electric and magnetic properties. One of the earlier investigated low dimensional molecular systems is K$_2$Pt(CN)$_4$Br$_{0.3}$·3H$_2$O (KCP) with high electric conductivity [1, 2]. Another compound of this kind is a charge-transfer complex Fe(C$_5$Me$_5$)$_2$·(TCNE) (Me = CH$_3$, TCNE = tetracyanoethylene), for which ferromagnetic ordering at low temperatures was reported [3]. A group of compounds with interesting magnetic properties are the complexes of copper, like Cu(py)$_2$Cl$_2$ [4, 5] or Cu(metronidazole)$_2$Cl$_2$·H$_2$O [6].

Many of the physical properties of single crystals are very sensitive to the presence of defects, impurities and/or disorder. It is important to note here that such perturbations are much stronger in low dimensional systems and are actually impossible to distinguish. However, there is some quantitative information about the disorder obtained from the study of single crystals using Mössbauer effect (ME) techniques [7–9].

In this paper we present the preparation and ME data of a new organometallic complex Fe(py)$_3$Cl$_3$·py (py = pyridine; referred to as FTPC-P), whose crystal and molecular structure at 190 and 290 K (Table 1) as well as magnetic susceptibilities and electrical conductivity measurement have been reported pre-

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TABLE 1. Crystallographic structure data of the Fe(py)$_3$Cl$_3$·py complex

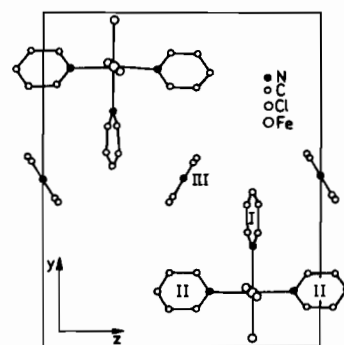| Crystal system	T (K)	Lattice parameters (Å)			Z
		a	b	c	
Monoclinic[a]	290	4.745(7)	14.395(9)	7.861(14)	2
Orthorhombic (C222$_1$)	190	8.861(2)	16.712(5)	14.280(4)	4

[a]$\beta = 93.93°$.

Fig. 1. Arrangement of molecules in low-dimensional FTPC-P crystal in the *bc* plane (yz).

viously [10–12]. The FTPC-P crystal has a very interesting and unique crystalline and molecular structure [10]. The pyridine ligands and pyridine molecules are packed in crossing stacks along the *b* and *c* axes of the crystal (Fig. 1). The Fe^{3+} ion is coordinated octahedrally by three Cl atoms and three N atoms

of the pyridine molecules (I and II, respectively Fig. 2).

Experimental

Preparation

The FTPC-P complex was synthesized by the direct reaction of anhydrous ferric chloride with pyridine in a one-to-four molar ratio [13]. Crystals of this complex were grown by slowly evaporating the solution of $Fe(py)_3Cl_3$ and pyridine. Then the crystals were dissolved again in pure pyridine and the saturated solution was left to stand in a tightly closed vessel for 48 h at 284 K. After this period of time the upper part of the solution was carefully decanted and a suitable nucleus of crystals was obtained. Crystal growth was performed in a crystallizer in a dark place at a constant temperature of 284 K. After a few weeks red–brown crystals with well-developed faces, of maximum size $30 \times 15 \times 7$ mm, were obtained. Their shape is shown in Fig. 3. The FTPC-P crystal was subjected to chemical analysis in order to determine its content as well as the oxidation number of iron. To determine the iron valency we used two selective analytical methods involving potassium fer-
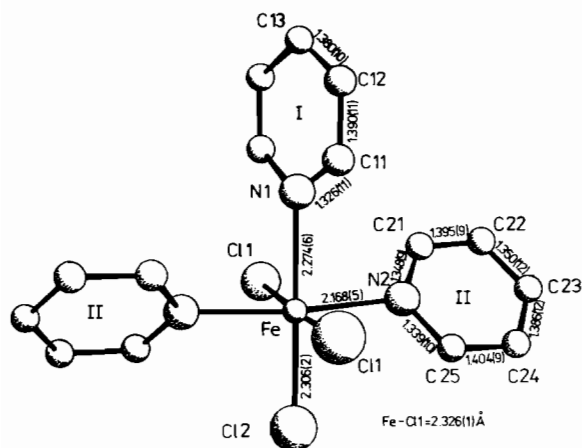

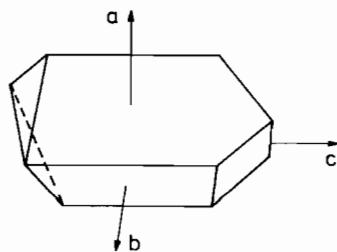Fig. 2. Molecular structure of $Fe(py)_3Cl_3$, a component of the FTPC-P complex.

Fig. 3. External configuration of the single crystal with crystallographic *abc* axes.

ricyanide and potassium ferrocyanide [14]. Quantitative determination of the ferric irons and chlorine ions in the sample was made by a complexometric method [15] and the Volhard method [16], respectively.

Apparatus and procedure

The ME measurements were performed on a SM-4T spectrometer [17, 18]. This spectrometer was equipped with a constant-acceleration transducer driven in the triangular mode, coupled with a 256 multi-channel analyser. The krypton-filled proportional counter was used to defect the 14.4 keV ^{57}Fe γ-rays. The number of counts per channel for each spectrum was about 10^6. Calibration of the velocity scale was made quite precisely using an ^{57}Fe armco iron absorber and a ^{57}Co-in-chromium source, both at room temperature. In the studies we used single crystals of the FTPC-P complex of high purity and crystals with a 0.1–1% order deficit of pyridine caused by high vacuum. The absorbant was placed in a leak-proof vessel and contained about 0.2 mg/cm^3 of Fe. The studies were performed at 290, 77 and 4.4 K. The ME spectra were analysed initially by the ME RKU computer program which was developed from the basic RKU program [19]. This program is particularly useful for spectra of poorly separated lines, as it enhances the line resolution of the experimental spectrum. The ME RKU program works well if the distances between particular lines are greater than their half widths. This program has been applied in other studies [17]. To determine other parameters of the ME spectrum, the least-squares method was employed.

Results and discussion

As a result of complex formation during the reaction of ferric chloride and pyridine, we obtained red–brown single crystals of melting point 315 K which is the same as the decomposition temperature of the compound. Using chemical and graviometric analysis the pyridine content of the complex was calculated and the summary formula $Fe(py)_4Cl_3$ was determined. Chemical analysis indicated that the iron in the complex occurs in the 3+ oxidation state. These results were confirmed by X-ray study [10] and magnetic susceptibility measurements [20]. The experimentally obtained results and literature data allowed us to distinguish two stages in the process of FTPC-P formation. In the first stage $Fe(py)_3Cl_3$ is obtained according to the reaction

$$FeCl_3 + 3py \longrightarrow Fe(py)_3Cl_3 + Q \qquad (1)$$
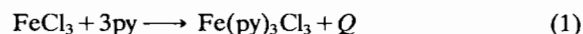
and a great amount of heat Q is liberated. The second stage of the reaction may be written as follows

$$Fe(py)_3Cl_3 + py \longrightarrow Fe(py)_3Cl_3 \cdot py \qquad (2)$$
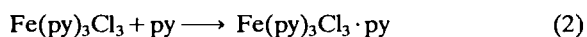
and it is not accompanied by heat liberation. The final product is a charge transfer complex (CTC) in the solid state consisting of two components: the ferric tripyridine chloride (FTPC) complex and a pyridine molecule (P) as shown in Fig. 1. FTPC [1] is composed of the ferric cation surrounded by six different ligands which form an octahedral coordinated complex and have C_2 molecular point group symmetry in the solid state (Fig. 2).

In $Fe(py)_3Cl_3$ each iron atom has as nearest neighbors two chlorine atoms at a distance of 2.326 Å and two nitrogen atoms (of the pyridine molecules) at 2.168 Å, with distortion from the planar configuration. There are also two neighboring chlorine and nitrogen atoms above and below the plane of this group at distances of 2.306 and 2.274 Å, respectively. These distances are greater than expected for a covalent bond [10]. This neutral complex, in which the ferric ion is the electron acceptor whereas pyridine is the electron donor, may belong to a group of either outer-orbital or inner-orbital complexes (Fig. 4). We can differentiate between these two cases by magnetic susceptibility measurements [20]. The experimental value of the effective magnetic moment is equal to $\mu_{eff} = 5.8$ μ_B, showing that FTPC is an outer-orbital ferric complex [20]. The CTC system is a compound obtained as a result of intermolecular interactions between the complex $Fe(py)_3Cl_3$ and the fourth pyridine denoted as III in Fig. 1, where the π electron plays a dominant role. More precisely, these interactions take place either between a ligated pyridine (I) and pyridine (III) along the c axis of the crystal, or between a ligated pyridine (II) and pyridine (III) along the b axis of the crystal. The smallest distances between two consecutive pyridines I and III or II and III are equal to 3.392 or 3.431 Å along the c or b axis of the crystal, respectively. These distances are comparable to the sum of van der Waals radii, which would testify to the presence of this type of interaction.

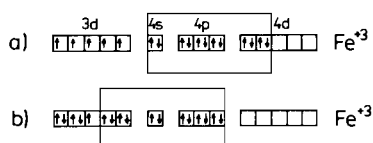ME absorption spectra of a single crystal of FTPC-P at various temperatures with the a axis of the

crystal parallel to the γ-ray beam direction are shown in Fig. 5. The ME spectra observed at temperatures of 290 and 77 K, i.e. in paramagnetic states are composed of an asymmetric quadrupole doublet. At 77 K the quadrupole splitting value is smaller by about 0.07 mm/s and the isomer shift is larger by 0.1 mm/s than the corresponding values obtained at 290 K. Moreover, at liquid nitrogen temperature an increase in γ-ray absorption by 7% was observed. At 4.2 K, as a result of Zeeman splitting of nuclear levels ^{57}Fe, six lines were obtained, which became visible on employing the ME RKU method [19]. At the same time a decrease in γ-ray absorption by 2% was observed when compared with the absorption at 77 K. The FTPC-P single crystal was also studied with the γ-ray beam propagating along the b or c axis. In both cases the ME spectra were composed of asymmetric doublets with inverse asymmetry only along the b axis. The obtained parameters of the Mössbauer spectra are presented in Table 2. It is worth noting that the quadrupole split spectra show asymmetrical line broadening just above the Néel temperature [21]. This may be explained by relaxation broadening [17]. However, the isomer shift values imply that the charge states of the Fe ions have a ferric character with high spin.

Figure 6 shows ME spectra for crystals with a deficit pyridine (pyridine non-stoichiometry). The
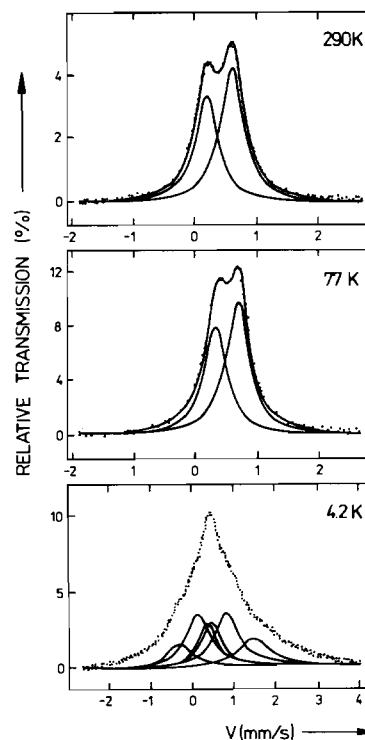

Fig. 4. Occupancy of orbits by electrons in outer-orbital (a) and inter-orbital (b) octohedral complexes of ferric ion.

Fig. 5. Mössbauer spectra of FTPC-P by γ-ray beam propagating along the a axis of a single crystal. The spectrum resolved by the ME RKU computer program only is depicted by a solid line.

TABLE 2. Mössbauer parameters of the Fe(py)$_3$Cl$_3$·py single crystal

γ-ray beam direction	T (K)	Isomer shift, δ^a (mm s^{-1})	Quadrupole splitting, ΔE (mm s^{-1})
a	290	0.38	0.44
b		0.38	0.44
a	77	0.48	0.37
a	42	0.47	
b		0.48	
c		0.47	

^{a}With respect to Armco iron.

TABLE 3. Mössbauer parameters of the Fe(py)$_3$Cl$_3$·py crystal with pyridine deficit

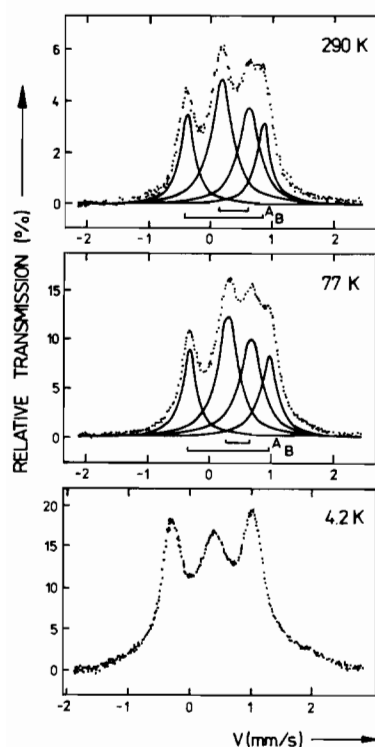| Quadrupole doublet	T (K)	Isomer shift, δ^a (mm s^{-1})	Quadrupole splitting, ΔE (mm s^{-1})
A	290	0.38	0.45
B		0.21	1.24
A	77	0.47	0.37
B		0.34	1.30
A	42	0.47	
B		0.34	1.31

^{a}With respect to Armco iron.

Fig. 6. Mössbauer spectra of FTPC-P crystal with a deficit of pyridine. The solid line denotes the result of application of computer program ME RKU.

ME spectra taken at 290 and 77 K are composed of two quadrupole doublets: one with a small quadrupole splitting denoted as A and the other denoted as B with a considerably greater splitting and smaller isomer shift. The parameters of the B doublet line at 4.2 K do not change, whereas the ones of the doublet A change similarly to those for the doublet in a stoichiometric crystal (Table 3). The above results obtained by ME measurements indicate that this complex which appears as a pure phase from X-ray diffraction, corresponds to the coexistence of tiny areas of a pyridine-deficient phase which results

in more distorted octahedral coordinated Fe^{3+} ions. The Mössbauer spectrum confirms this; in addition the doublet A characteristic of a single crystal of high purity also shows a doublet B. The presence of a doublet B in the FTPC-P crystal spectrum unambiguously indicates a deviation from the single phase crystal already when the decrease of pyridine is in the order of 0.1% within the temperature range 4.2–290 K. Due to the application of the ME method it was proven that the low dimensional FTPC-P complex we obtained is a perfectly ordered single phase crystal.

Conclusions

Reaction of anhydrous ferric chloride with pyridine resulted in the formation of complex compound whose formula was Fe(py)$_3$Cl$_3$·py. Crystals of the complex may be obtained from a pyridine solution at room temperature. The FTPC-P compound consists of an organometallic complex of Fe(py)$_3$Cl$_3$ and a pyridine molecule. These components make up a CT complex. In the complex, iron with high spin occurs at the 3+ oxidation state. FTPC-P crystals may occur in two crystallographic systems: orthorhombic and monoclinic with the structural phase transition at a temperature close to 200 K. Application of the ME method for determination of pyridine stoichiometry, spin and oxidation states of iron in single crystals of FTPC-P in a wide range of temperature proved to be very successful.

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