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UNLOCKING THE FUNCTIONAL POTENTIAL OF BIS(PHENYLHYDRAZONES): SYNTHESIS AND STRUCTURAL ELUCIDATION OF THE FIRST FE(II) COMPLEX WITH A 2,6-DIACETYLPYRIDINE-BASED LIGAND

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Abstract: The reaction of a warm methanolic solution of iron(II)-bromide and an acetone solution of 2,6-diacetylpyridine-bis(phenylhydrazone) (L) gave dark red prismatic single crystals of the complex $[FeL_2]Br_2$. The composition and purity were elucidated *via* elemental analysis, and the coordination mode was determined based on FTIR spectra. The latter was confirmed by X-ray structural analysis. This complex is isostructural with previously synthesized complexes $[CuL_2]Br_2$ and $[CoL_2]I_2$ – all three complexes crystallize in the *C*2/*c* space group and have very similar unit cell parameters. $[FeL_2]^{2+}$ lies on a two-fold rotation axis; thus, the asymmetric unit consists of one ligand molecule, a half of the Fe(II) ion, and one bromide ion. Fe(II) is situated in a very distorted octahedral environment formed by six nitrogen atoms of two ligand molecules, with *trans*-angles having the values of 146.81° and 173.43°. Due to steric factors, the phenyl rings of the ligand are twisted, which can be seen from the torsion angles of 141.42° for one and 155.27° for the other phenylhydrazone moiety. Besides, the complex is characterized by coupled TG-MS measurements.

Keywords: metal complexes, hydrazones, synthesis, characterization.

1. INTRODUCTION

Thanks to their excellent chelating properties and notable pharmacological potential, hydrazone-type ligands have attracted considerable attention over the past decades — and continue to do so today [1–7]. These compounds have been widely explored as highly selective analytical reagents, luminescent probes, and molecular sensors [8]. Additionally, numerous studies have demonstrated their significant antibacterial, antifungal, and antitumor activities [9 –13], with certain derivatives proposed as promising agents for the treatment of genetic and neurodegenerative disorders, such as thalassemic syndrome and Alzheimer's disease [14–17].

A particularly important class of compounds includes 2,6-disubstituted pyridine derivatives, which exhibit a wide range of biological and catalytic properties, such as anti-inflammatory, antitumor, analgesic [18], antimicrobial [19], and catalytic activity [20, 21]. Among them, 2,6-diacetylpyridine stands out as a key diketone precursor in the synthesis of both symmetric and asymmetric derivatives, especially due to the development of efficient one-pot synthetic procedures [22]. Bis(hydrazones) of 2,6-diacetylpyridine are of special interest due to their versatile denticity—ranging from tridentate to heptadentate—and rich coordination behavior and possible application [23]. Despite the considerable number of metal complexes synthesized with these

ligands, structurally characterized bis(ligand) complexes are still relatively rare [24]. In particular, the symmetric bis(phenylhydrazone) derivative of 2,6-diacetylpyridine (L) has shown promise due to its interesting electronic properties and potential biological activity, making it a suitable candidate for applications in sensor development and functional materials. Only a few metal complexes of this ligand have been characterized, including Cu(II), Co(II), and Cr(III) complexes [25-29], with both mono- and bis(ligand) forms reported. In these complexes, the ligand acts as a tridentate coordinating *via* pyridine and two imine nitrogen atoms in its neutral or monoanionic form.

Given that the presence of a metal center often enhances both the physicochemical and biological properties of organic ligands, further exploration of the coordination potential, structure, and function of such metal complexes remains a compelling field of research. Thus, here we report the synthesis and structure of the complex $[FeL_2]Br_2$.

2. EXPERIMENTAL

2.1. Materials and methods

All chemicals used were commercial products of analytical reagent grade, except for the ligand, which was synthesized by the previously reported procedure, *i.e.*, by refluxing the ethanolic solution of 2,6-diacetylpyridine and phenylhydrazine-hydrochloride, in the presence of $LiOAc{\cdot}2H_2O$ [26]. The structure of the ligand was confirmed later by isolating single crystals suitable for X-ray crystallographic analysis by diffusion of Et_2O to a concentrated acetonic solution of the ligand [28]. Elemental analyses (C, H, N) of the air-dried complexes were performed using standard micro-methods on an Elementar vario EL III. Molar conductivity of freshly prepared complex solution ($c = 1\times10^{-3}$ mol dm^{-3}) was measured on a Jenway 4510 conductivity meter. IR measurements were recorded on a Thermo Nicolet iS20 FTIR spectrophotometer in ATR mode (range 4000 – 400 cm^{-1}). Melting points were measured on a Nagema melting point microscope Rapido. Magnetic susceptibility measurements were conducted at room temperature on an MSB-MKI magnetic susceptibility balance, Sherwood Scientific Ltd., Cambridge. The simultaneous thermogravimetric-differential scanning calorimetric (TG-DSC) analysis was conducted on an SDT Q600 simultaneous thermal analyzer from TA Instruments. The sample mass was about 3 mg in an open alumina crucible. The reference was an empty, open alumina crucible. Heating rate: 10 K/min,

Table 1. *Selected crystallographic and refinement details for the complex.*

Crystal Data		*Data collection*	
Chemical formula	$C_{42}H_{42}Br_2FeN_{10}$	Absorption correction	Analytical
M_r	902.52	T_{min}	0.411
Crystal system	Monoclinic	T_{max}	0.667
Space group	*C*2/*c*	Measured reflections	24044
Temperature, K	170(2)	Independent reflections	3911
a / Å	20.8485(12)	Observed reflections [$I>2\sigma(I)$]	3279
b / Å	15.3911(9)	R_{int}	0.0409
c / Å	11.9226(8)	$(\sin\theta/\lambda)_{max}$ / Å^{-1}	0.625
β / °	92.239(5)	*Refinement*	
V / Å^3	3822.8(4)	R [$F^2 > 2\sigma(F^2)$]	0.0267
Z	4	wR [F^2]	0.0609
Radiation type	Mo $K\alpha$	*S*	1.044
μ / mm^{-1}	2.532	Reflections	3911
Crystal size, mm	0.32 × 0.28 × 0.25	Parameters	259

purge gas: argon, flow rate: 50 mL/min. The measurement was performed from room temperature up to 700 °C. The TG-MS measurements were done on an online coupled mass spectrometer HPR20 from Hiden Analytical using an electron impact ionization. The selected ions between *m/z* = 14 and 135 were analyzed in Multiple Ion Detection (MID) mode. SC-XRD experiments were performed on a four-circle single crystal X-ray diffractometer Gemini S (Oxford Diffraction), equipped with a position-sensitive CCD detector Sapphire3 and with a Mo Kα X-radiation (λ = 0.71073 Å) source. Measurements were carried out at low temperature (170 K) using a cryostream device to reduce thermal motion and improve resolution. Instrument control and initial data reduction were performed using *CrysAlisPro* [30]. Absorption corrections were applied through analytical integration of absorption equations based on a multifaceted crystal model [31]. The crystal structure was solved using *ShelXle* [32] and further visualized and analyzed with *Mercury* [33] and *PublCIF* [34]. Crystallographic and refinement data are summarized in Table 1.

2.2. Synthesis of the complex

The solution of 0.2 mmol (58 mg) L in 3 cm^3 of acetone was added to the solution of 0.2 mmol (44 mg) of iron(II)-bromide in 5 cm^3 of methanol. The reaction mixture was refluxed for 30 minutes and left to evaporate at room temperature. After three days, dark red, prismatic single crystals were filtered off and washed with methanol. Yield: 58 mg (32 %).

Anal. Calcd. for $C_{42}H_{42}N_{10}Br_2Fe$ (Mr = 902.52): C, 55.89; H, 4.69; N, 15.52 %. Found: C, 56.13; H, 4.82; N, 15.16 %. λ_M(DMF) = 54 S cm^2 mol^{-1}. IR bands [cm^{-1}]: 3151, 3096, 2989, 2939, 1593, 1542, 1517, 1491, 1437, 1379, 1330, 1302, 1254, 1214, 1167, 1119, 1089, 1023, 880, 807, 735, 692, 661, 631, 616, 555, 514, 498, 468.

3. RESULTS AND DISCUSSION

3.1. Synthesis and physicochemical properties of the complex

By refluxing a warm methanolic solution of iron(II) bromide with an acetone solution of 2,6-diacetylpyridine-bis(phenylhydrazone) (L) in a molar ratio 1:1, dark red prismatic single crystals of the complex $[FeL_2]Br_2$ were obtained (Figure 1). Although the metal-to-ligand molar ratio was 1:1, a bis(ligand) complex was obtained, as it was expected based on previously reported synthetic procedures of the complexes with this ligand.

The synthetic routes to the known complexes with this ligand are shown in Figure 2. So far, only three metal complexes with this ligand have been synthesized in the form of single crystals, thus structurally characterized. The reaction of copper(II)-bro-

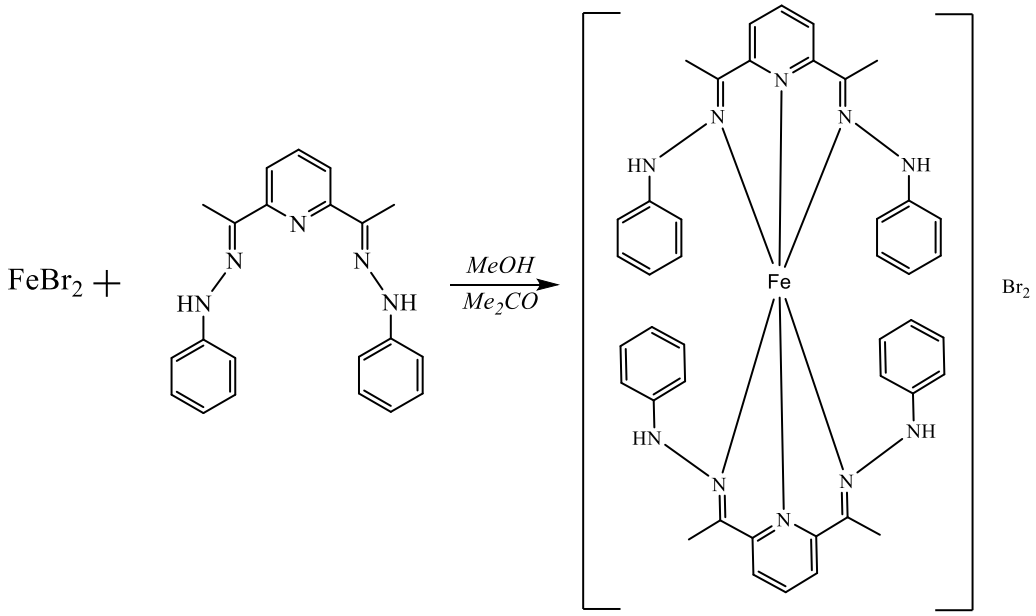

Figure 1. *Synthesis of the complex* $[FeL_2]Br_2$

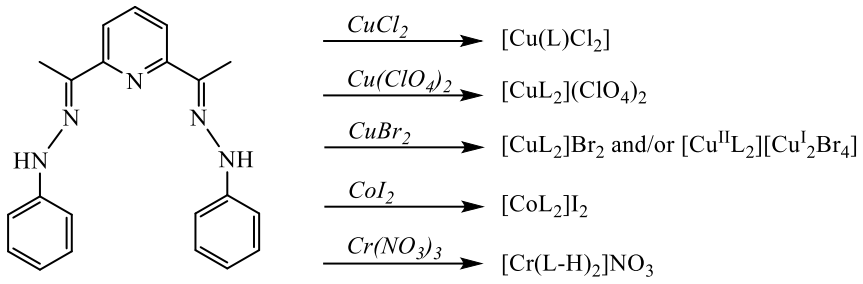

Figure 2. *Structural formula of the ligand and coordination formulas of its metal complexes*

mide and the ligand yielded in the formation of single crystals of the complex $[CuL_2]Br_2$, the complex $[Cu^{II}L_2][Cu^{I}_2Br_4]$, or their mixtures [27, 28], depending on the mole ratio of the reactants and the nature of the solvent used. When an ethanolic solution of cobalt(II)-iodide was used, the analogous complex of the formula $[CoL_2]I_2$ was obtained [26]. Aside from these, the synthesis of one mono(ligand) complex, $[Co(L)Cl_2]$ as well as bis(ligand) complex, $[ML_2](ClO_4)_2$, was reported [24]. Their formulas were proposed based on spectral and elemental analysis. Finally, in the reaction of metanolic solutions of $Cr(NO_3)_3$ and the ligand, red needles of the complex $[Cr(L–H)_2]NO_3$ were obtained, in which a novel, anionic form of the coordinated ligand was suggested [29] (Figure 2).

The isolated complex is stable in air and at elevated temperatures, soluble in methanol and DMF, and almost insoluble in H_2O, ethanol, acetonitrile, and acetone. The molar conductivity of the complex in DMF corresponds to that of a 1:1 electrolyte [35]. Although the formula $[FeL_2]Br_2$ suggests a 2:1 electrolyte, the lower observed value in DMF can be attributed to the bulky nature of the complex cation, which reduces its ionic mobility in this less polar, aprotic solvent. In addition, incomplete dissociation in DMF may contribute to the effective 1:1 behavior.

Comparing the FTIR spectra of the complexes (Figure 3), the coordination of the ligand can be confirmed. The most prominent differences are observed in the region 1600–1350 cm^{-1}. Upon coordination of the imine groups, the band at 1563 cm^{-1} in the free ligand shifts to 1517 cm^{-1} in the complex, indicating a negative shift due to metal binding [25, 36].

The band at 3155 cm^{-1}, attributed to the ν(N–H) stretching vibration of the pyridine ring, is no longer observed in the spectrum of the complex, which suggests deprotonation and coordination *via* the nitrogen atom. Other high-frequency bands in the 3100–2940 cm^{-1} region, corresponding to ν(C–H) vibrations of methyl groups and aromatic rings (pyridine and benzene), do not significantly shift upon coordination but show differences in intensity. Additionally, the bands observed at approx-

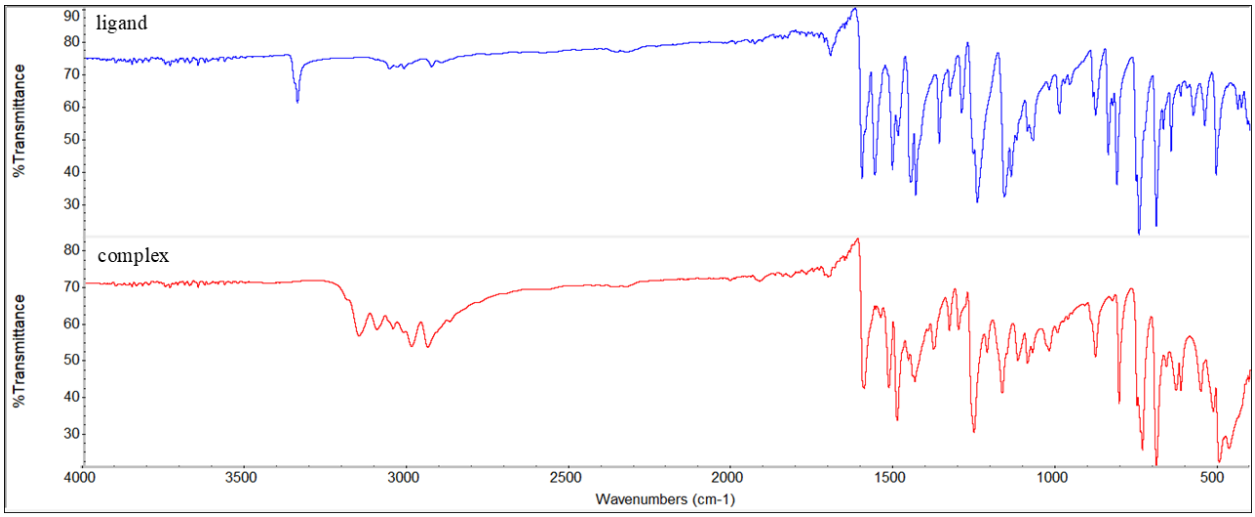

Figure 3. *FTIR spectra of the ligand and the complex*

imately 1600 and 1500 cm^{-1} in both spectra can be attributed to aromatic ring stretching vibrations, involving delocalized C–C and C–N bonds in the pyridine and benzene rings. These bands show mild shifts upon coordination of the pyridine nitrogen (for ca. 10-15 cm^{-1}) [37].

3.2. Molecular and crystal structure of the complex

The asymmetric unit of the complex (Figure 4a) consists of one half of an iron(II) ion, the ligand molecule, and one bromide ion. Iron(II) is situated in a distorted octahedral environment (Figure 4b) of two tridentate ligand molecules, both of them coordinated in the usual NNN manner, through pyridine, and two azomethine nitrogen atoms. This leads to the formation of four five-membered chelate rings.

The value of trans-angle N1–Fe–N1^{i} deviates slightly, while the N2–Fe–N4 deviates significantly from the theoretical 180°, indicating the deformation ligand molecules undergo to form a *bis*(ligand) complex. Also, while the free ligand is almost planar [26, 28], a significant deviation from planarity is observed in the complex, which can be described by the values of torsion angles given in Table 2.

All intra-ligand bond lengths and angles are in concordance with the previously reported structure of the ligand and the complexes [26-28]. Due to coordination, N2–N3 and N4–N5 bonds are slightly longer in the complex than in the free ligand, while the angles C6–N2–N3, C8–N4–N5, N1–C1–C6, and N1–C5–C8 are narrowed. The metal–ligand bond lengths are within the expected range and are consistent with those typically observed in the complexes with this ligand. The bond to the pyridine nitrogen atom is the shortest, while the bonds to the imine nitrogen atoms are notably longer.

Table 2. *Selected bond distances and angle values*

Bond	Distance, Å	Angle	Value, °
Fe1–N1	2.0805(15)	C1–N1–C5	120.37(16)
Fe1–N2	2.2342(16)	N1–C1–C6	115.10(17)
Fe1–N4	2.3507(15)	N1–C5–C8	115.11(16)
N1–C1	1.349(2)	C1–C6–N2	115.87(17)
N1–C5	1.343(2)	C5–C8–N4	115.21(17)
C1–C6	1.471(3)	C6–N2–N3	116.64(16)
C5–C8	1.472(3)	C8–N4–N5	115.04(16)
C6–N2	1.296(2)	N2–N3–C10	119.31(16)
C8–N4	1.297(2)	N4–N5–C16	120.77(17)
N2–N3	1.370(2)	N1–Fe–N2	74.33(6)
N4–N5	1.373(2)	N1–Fe–N4	72.48(6)
N3–C10	1.401(3)	N2–Fe–N4	146.81(6)
N5–C16	1.392(3)	N1–Fe–N1^{i}	173.43(8)
Torsion angle		Value, °	
C2–C1–C6–N2	177.67(18)	N2–N3–C10–C11	-41.8(3)
C4–C5–C8–N4	156.60(18)	N4–N5–C16–C17	-28.7(3)
C6–N2–N3–C10	169.29(18)	N2–N3–C10–C15	141.4(2)
C8–N4–N5–C16	164.56(17)	N4–N5–C16–C21	155.27(18)

Symmetry operation: (i):1–x, y, 1/2–z

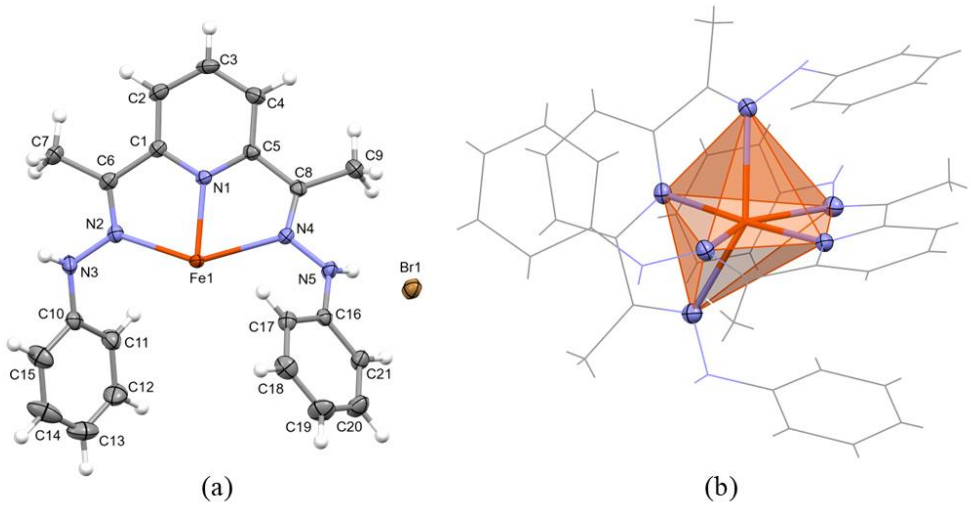

Figure 4. *Asymmetric unit of the complex and labeling scheme (a) and coordination polyhedron (b)*

Both H-donors of the ligand, *i.e.*, N3 and N5 atoms, form the hydrogen bonds with the bromide as acceptor. The parameters of these bonds are very similar to those found in the structure of $[CuL_2]Br_2$ [27]. The same applies to the crystal packing of the structural units of the complex (Figure 5).

3.3. Thermal properties of the complex

The thermal properties of the complex were examined by simultaneous thermogravimetric-differential scanning calorimetric (TG-DSC) analysis in argon. The complex is stable up to about 140 °C, onset (Figure 6). However, a very small mass loss

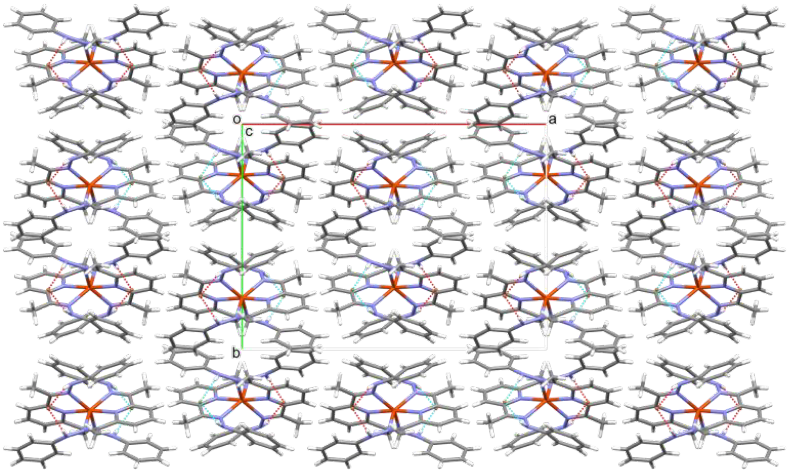

Figure 5. *Crystal structure of the complex viewed along the c-axis*

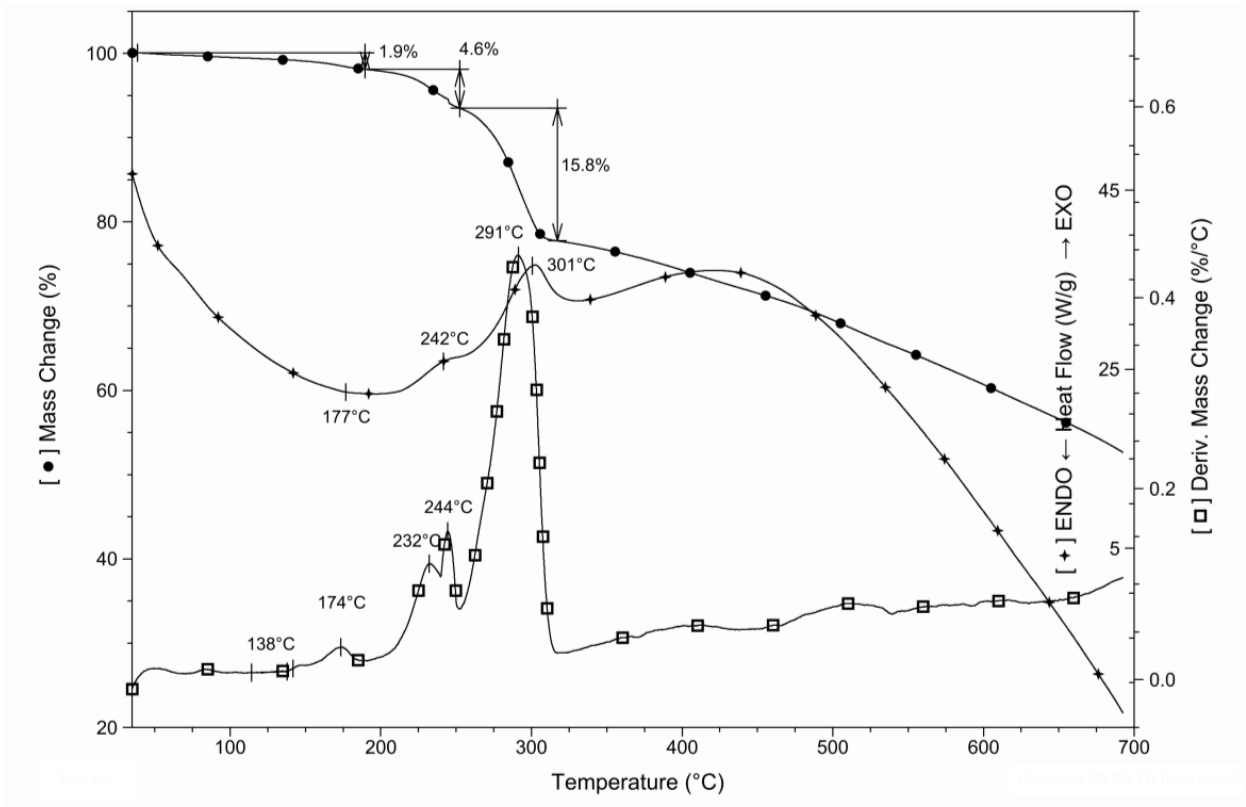

Figure 6. *TG (●), DTG (□), and DSC (+) curves of $[FeL_2]Br_2$ in argon*

can be observed from room temperature up to the onset temperature. This mass loss at higher temperatures became more intense, and a discreet mass loss step (1.9 %) can be distinguished with a DTG maximum at 174 °C. Considering the crystal structure of the compound, which does not contain lattice solvent, this mass loss is most probably caused by the evaporation of some absorbed moisture. Above 190 °C, the thermal decomposition of $[FeL_2]Br_2$ occurs in several overlapped steps. Just two decomposition steps can be distinguished by DTG maxima at 232 °C (the apparent peak at 244 °C results from a small trembling of the balance beam, thus these two peaks are analyzed as one) and 291 °C. Above this temperature, the decomposition rate slows down but is not finished up to 700 °C. The first detected heat effect is a wide endothermic peak with a maximum at 177 °C, which corresponds to the evaporation of the absorbed moisture. The next two steps are followed by a slightly exothermic and an exothermic heat effect with peak maxima at 242 and 301 °C.

To get a better insight into the decomposition mechanism, online coupled TG-MS measurements were conducted. The first, very slight mass loss in a wide temperature range also gives a weak change in the signals *m/z* 18 and 17, thus proving the evaporation of moisture absorbed during storage (Figure 7). Besides, a slight change can also be observed on the *m/z* 16 signal, which can correspond to NH_2^+ or CH_4^+ fragments. Since the compound is synthesized in a methanol/acetone solution, the CH_4^+ fragment evolution is more probable at low temperatures than NH_2^+, which is a less probable fragment from the diphenylhydrazone-type ligand. Namely, based on the TG, DTG, and DSC curves, and the structure of the ligand, its decomposition and the formation of NH_2^+ fragments at somewhat above room temperature is very unlikely. The evaporation of the rest of the solvent traces is more possible. Here, we need to highlight that only trace amounts of moisture and the solvents used are absorbed. Above 200 °C, the decomposition of the compound occurs, proved by fragments of *m/z* 16 (NH_2^+), 17 (OH^+), 18 (H_2O^+), 28 (N_2^+, CH_2N^+, or $C_2H_4^+$, and N_2^+ from the background), 30 ($H_2N_2^+$, CH_4N^+, or $C_2H_6^+$), 32 ($H_4N_2^+$ and O_2^+ from the background), 44 ($H_2N_3^+$, $CH_4N_2^+$, $C_2H_6N^+$, or $C_3H_8^+$).

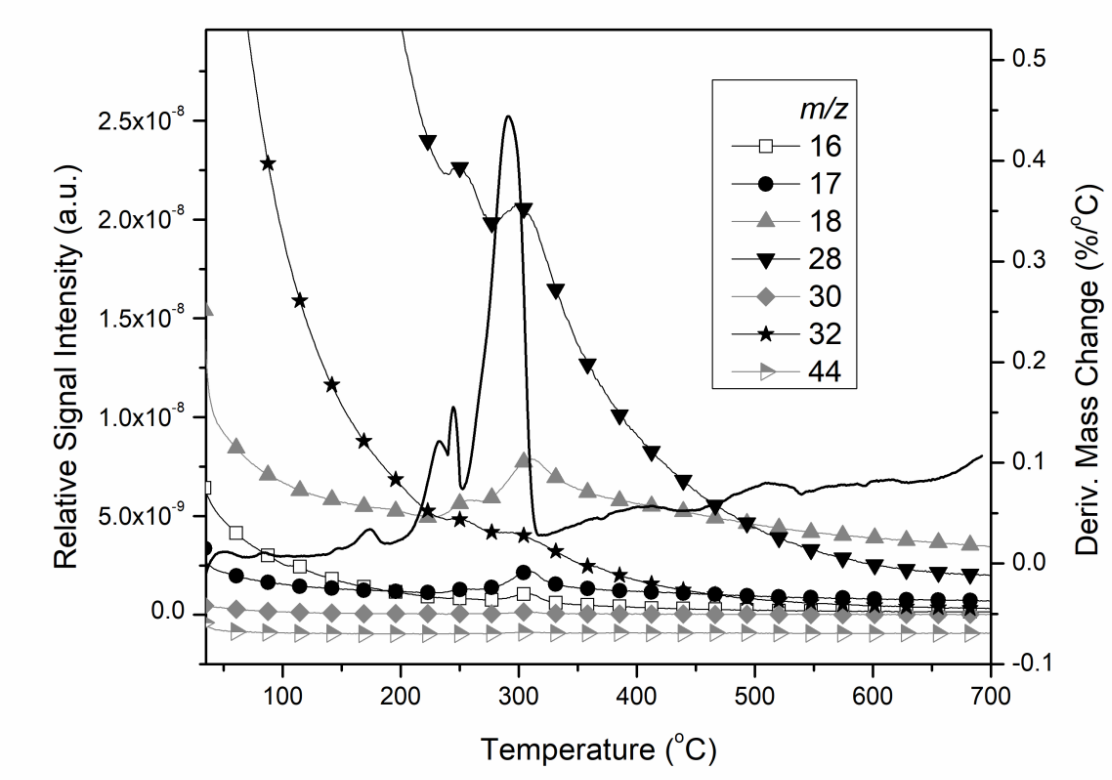

Figure 7. *Selected ion current curves of* $[FeL_2]Br_2$ *recorded in argon*

4. CONCLUSION

The new complex compound, $[FeL_2]Br_2$, is obtained in the reaction of the symmetric bis(phenylhydrazone) derivative of 2,6-diacetylpyridine (L) with $FeBr_2$. Even from the reaction mixture of $FeBr_2$ and L in a molar ratio of 1:1, a *bis*(ligand) compound crystallized. The molar conductivity data suggest that $[FeL_2]Br_2$ behaves as a 1:1 type electrolyte due to the reduced mobility of the bulky cation and only partial dissociation of the complex salt. The FTIR spectra of the ligand and the complex show the changes caused by the coordination of L to the Fe(II) ion. $[FeL_2]Br_2$ is isostructural with earlier synthesized complexes $[CuL_2]Br_2$ and $[CoL_2]I_2$. Since the L is voluminous, its deformation in the *bis*(ligand) complexes was expected. Accordingly, Fe(II) is situated in a distorted octahedral environment with shorter $Fe–N_{pyridine}$ and longer $Fe–N_{azomethine}$ bonds. The thermal analysis data prove the presence of some absorbed moisture. During the thermal decomposition, $[FeL_2]Br_2$ loses only about 20 % of its mass up to about 330 °C in several partially separated steps, followed by exothermic heat effects. The rest of the compound decomposes more slowly, at a steady rate without any other distinguishable decomposition step. These results represent an initial step toward unlocking the full potential of 2,6-diacetylpyridine-based complexes. They point to their promise as candidates for diverse applications and the need for further detailed studies to fully explore their properties and possible functionalities.

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ПРВИ Fe(II) КОМПЛЕКС СА БИС(ФЕНИЛХИДРАЗОНСКИМ) ЛИГАНДОМ: СТРУКТУРНА АНАЛИЗА У КОНТЕКСТУ ОДНОСА СТРУКТУРА-СВОЈСТВА

Сажетак Реакцијом топлог метанолног раствора гвожђе(II)-бромида са ацетонским раствором лиганда бис(фенилхидразона) 2,6-диацетилпиридина (L) добијени су мрки призматични монокристали комплекса формуле $[FeL_2]Br_2$. Састав и чистоћа производа потврђени су резултатима елементалне анализе. Комплекс је окарактерисан FTIR спектроскопијом, на основу које је претпостављена тридентатна координација хидразонског лиганда, а што је потврђено и рендгенском структруном анализом. Овај комплекс изоструктуран је са раније синтетисаним комплексима $[CuL_2]Br_2$ и $[CoL_2]I_2$, кристалише у *C*2/*c* просторној групи и има сличне параметре јединичне ћелије. Комплексни катјон $[FeL_2]^{2+}$ смештен је на оси ротације другог реда, па асиметричну јединицу чини један молекул лиганда, половина Fe(II) јона и један бромидни јон. Јон Fe(II) смештен је у веома деформисаном октаедарском окружењу шест донорних атома азона два молекула лиганда са вриједностима *trans*-углова од 146,81° и 173,43°. Због стерних ограничења дошло је до увртања фенилних прстенова, те одговарајући торзиони углови износе 141,42°, за један фенилхидразонски остатак, односно 155,27° за други. Комплекс је окарактерисан и спрегнутим TG-MS мерењима.

Кључне ријечи: комплекси метала, хидразони, синтеза, карактеризација.

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