

Structural Study, Vibrational, Optical, Thermal Properties and Hirshfeld Surface Analysis of a New Iron (III) Complex: FeCl₄(C₅N₂H₆)(C₅N₂H₅)

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Abstract

The title compound, $\text{FeCl}_4(\text{C}_5\text{N}_2\text{H}_6)(\text{C}_5\text{N}_2\text{H}_5)$ consists of two $[(\text{C}_5\text{N}_2\text{H}_6)(\text{C}_5\text{N}_2\text{H}_5)]^+$ organic cations and $[\text{FeCl}_4]^-$ anion. The geometry of the iron ion is tetrahedral, formed by four chlorine atoms. The complex was characterized by single crystal X-ray diffraction, Fourier Transform Infrared spectroscopy, thermal analysis and UV-Visible spectroscopy. Hirshfeld surface analysis was also used for understanding the intermolecular interactions in the crystal packing. Single-crystal X-ray diffraction analysis indicates that this complex crystallizes in the monoclinic system, P2₁/c space group with a = 7.598 (3) Å, b = 13.694 (4) Å, c = 17.105 (5) Å, $\beta = 97.203$ (6)° V = 1765.7 (10) Å³ and Z = 4. The [FeCl₄]⁻ anion and [(C₅N₂H₆)(C₅N₂H₅)]⁺ cations are linked through three-dimensional hydrogen-bonding network consisting of N-H…Cl and π - π interactions. Hirshfeld surface analysis and the related 2D fingerprint plots reveal that the complex is dominated by N-H…Cl contacts.

Keywords

Complex, Crystal Structure, X-Ray Analysis, Optical Study, Thermal Analysis, Hirshfeld Surface

1. Introduction

The research into coordination chemistry of iron complexes with Schiff-base ligands has given rise to materials exhibiting coexistence of novel properties due to the interaction between the subnetworks.

The iron-based compounds are very interested due to their broad applications in catalysis, biology, medicine and even in agriculture [1]-[6]. On the other

hand, pyridine derivatives are attracting increasing interest in agrochemical and pharmaceutical [7] [8]. Indeed, hydrogen-bonding is necessary for the design and development of multifunctional hybrid compounds [9] [10]. In order to extend our studies in this field, we have focused on the combination of 3-amino-2-chloropyridinium ligand with iron metal ion to constitute suitable building blocks in generating a variety of supramolecular assemblies through the hydrogen bond interactions. Furthermore, the application of Hirshfeld surface analysis is increasing in the crystallography, providing a visual picture of intermolecular interactions and of molecular shapes in a crystalline environment. We report in this present study the synthesis, structural characterization by single crystal X-ray diffraction and X-ray powder diffraction, vibrational study by infrared spectroscopy, optical properties and thermal analyses of a new iron (III) complex. The intermolecular contacts in the crystal were investigated by Hirshfeld surface analysis.

2. Materials and Measurements

2.1. Experimental

All reagents and solvents were purchased from Sigma Aldrich and used without further purification. Infrared spectrum on KBr pellets of the hybrid compound was obtained using Perkin Elmer Spectrum spectrophotometer in the range of 4000 - 400 cm⁻¹. The UV-visible spectrum was recorded on a 2802 UV/VIS spectrophotometer (UNICO) within the range 200 - 800 nm. X-ray powder diffraction measurements were collected on a BRUKER D8 ADVANCE X-ray diffractometer using K*a*1 (Cu) (λ = 15.406 Å) radiation. Differential thermal analysis (DTA) was carried using SETARAM-TG-DTA 92-16 microthermobalance and Thermogravimetric (TG) measurement was carried out on a SETARAM SETSYS Evolution-1750 microthermobalance with an alumina tube furnace and a graphite heater.

2.2. Synthesis of (3-Amino-2-Chloropyridinium) Tetrachloridoiron (III) FeCl₄(C₅N₂H₆)(C₅N₂H₅)

3-Amino-2-chloropyridinium (0.5 mmol·128.56 mg) was dissolved in 5 mL of methanol (solution A). Anhydrous iron chloride (III) (0.33 mmol·162.2 mg) was dissolved in 5 mL of methanol (solution B). The A solution was added dropwise in B solution, resulting in yellow solution. The reaction mixture was stirred at room temperature for 30 minutes. Then, red prismatic crystals suitable for X-ray diffraction were obtained after 3 weeks of slow evaporation at room temperature.

2.3. Single Crystal X-Ray Structural Analysis

A red prismatic crystal of size $(0.42 \times 0.28 \times 0.21)$ was carefully selected for the structural analysis. The raw diffraction data were collected at 298 K with Enraf-Nonius CAD4 automatic four-circle equipped with graphite monochro-

mator using Mo K*a* radiation ($\lambda = 0.71073$ Å) [11]. The structure was solved using the SIR 2014 program [12] refined by full-matrix least squares technique on F2 through SHELXL-2014 [13]. The non-hydrogen atoms were inserted anisotropically while the hydrogen atoms were fixed using AFIX 43 instruction, C-H = 93 Å and N-H = 86 Å. An empirical psi-scan [14] absorption correction was applied ($T_{min} = 0.694$, $T_{max} = 0.999$).

The crystallographic data, the experimental details of the data collection and the results of refinement of the crystal structure are presented in **Table 1**.

DIAMOND version 3.2 program [15] was used for molecular graphics.*CIF file containing complete information about the structure of $\text{FeCl}_4(\text{C}_5\text{N}_2\text{H}_6)(\text{C}_5\text{N}_2\text{H}_5)$ was deposited with the Cambridge Crystallographic Data Center (CCDC 2056579). The data can be obtained free of charge from the following website: http://www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

3.1. Crystal Structure of the Complex

 $\operatorname{FeCl}_4(C_5N_2H_6)(C_5N_2H_5)$ crystallizes in the monoclinic system with space group $\operatorname{P2}_1/c$. The asymmetric unit of the complex is made up of two independents $[(C_5N_2H_6)(C_5N_2H_5)]^+$ organic cations, one $[\operatorname{FeCl}_4]^-$ tetrahedral as illustrated in **Figure 1**.

Table	1.	Crystal	and	structure	refinement	data	for	the	title	compound:
FeCl ₄ (C ₅ N	$(C_5)^{1}$	N_2H_5							

4(-5) 2 87(-5) 2 57	
Chemical formula	$FeCl_4(C_5N_2H_6)(C_5N_2H_5)$
Formula weight (g·mol ^{−1})	455.78
Temperature (K)	298
Crystal system; Space group	Monoclinic; P2 ₁ /c
a (Å); b (Å); c (Å); β (°)	7.598 (3); 13.694 (4); 17.105 (5); 97.203 (6)
Volume (Å3); Z	1765.7 (10); 4
Sample size (mm)	$0.42\times0.28\times0.21$
Radiation, λ , (Å)	$\lambda = 0.71073$
$\mu (\mathrm{mm}^{-1})$	1.76
F000	908
hetaRange (°)	$2.4 \le heta \le 27.2$
Scan mode	ω -2 θ
Absorption correction	psi-scan
$\mathrm{T}_{\mathrm{min}}$, $\mathrm{T}_{\mathrm{max}}$	0.694, 0.999
Number of reflections measured;	4747
Independent reflections; R _{int}	3806; 0.038
Reflections with $[I > 2\sigma(I)]$	1934
R (F ²); <i>ω</i> R (F ²); S (GOOF)	0.051; 0.140; 0.98
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ (e Å ⁻³)	0.50; -0.34



Figure 1. Asymmetric unit of $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$.

The central atom of the anionic moiety is tetracoordinated by four chlorine atoms (Cl02 Cl04 Cl05 and Cl07). FeCl₄ is characterized by a range of Fe-Cl bond length from 2.181 (7) Å to 2.187 (7) Å and the Cl-Fe-Cl angles vary from 107.882 (3)° to 111.989 (3)° They are comparable with the values reported for similar compounds containing the FeCl₄ [16] [17]. Therefore, the calculated average values of the distortion indices as described by Baur [18] corresponding to the different angles and distances in FeCl4 tetrahedra, (DI(Cl-Fe-Cl) = 0.00157° and DI(Fe-Cl) = 0.00301 Å; show a light distortion. The 3-amino-2-chloropyridinium ligand is planar and the average C-C (1.373(3) Å), C-N (1.705 (5) Å) and C-Cl (1.339(4) Å) bond lengths, and the average angles (130.565 (14)) within the rings are in a good agreement with those admitted for a 3-amino-2-chloropyridinium coordinated metal complexes [19].

The crystal structure of the complex $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$ can be described as an alternation of layers between organic cations and inorganic anions into lines running along the [010] direction Figure 2.

The anions $[FeCl_4]^-$ are located between the cations layer along the [001] direction (**Figure 3**).

The $[FeCl_4]^-$ and $(C_5N_2H_6)^+$ are connected via N-H···Cl hydrogen bonds that link the amino N-H group to the Cl atoms, forming a cations-anions interaction type by connecting the positive and the negative layers and reinforcing the cohesion of the ionic structure (**Figure 4**).

An additional stability of the crystal is afforded by π - π interaction between the aromatic rings of the cations $[(C_5N_2H_6) (C_5N_2H_5)]^+$ are found to be 3.739 Å **Figure 5**.

3.2. X-Ray Powder Diffraction

The phase purity of our complex was checked by the Rietveld refinement. The



Figure 2. Projection of $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$ structure along the b axis.



Figure 3. Projection of $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$ structure along the c axis.



Figure 4. Fragments of $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$ the molecular structure of showing hydrogen bonding interactions.



Figure 5. Representation of the cationic cycles and the interactions π - π .

single crystal structure was used as a starting model. The refinement was performed using the GSAS-EXPGUI software [20] [21]. The result is fully consistent with the obtained from the single crystal diffraction data. All diffraction peaks were indexed in P2₁/c space group and no additional peaks were observed. This clearly indicates the purity of our phase FeCl₄($C_5N_2H_6$)($C_5N_2H_5$) (Figure 6).



Figure 6. Experimental and calculated powder X-ray diffraction patterns of $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$.

3.3. IR Spectrum

To gain more information on the functional groups present in the complex, we have used the infrared spectroscopy technique. The IR spectrum of the compound $\text{FeCl}_4(\text{C}_5\text{N}_2\text{H}_6)(\text{C}_5\text{N}_2\text{H}_5)$ recorded at room temperature in the region 400 - 4000 cm⁻¹ is depicted in **Figure 7**.



Figure 7. IR spectrum of the compound $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$.

In the region 3700 - 2700 cm⁻¹ the broad and strong bands are indicative of intermolecular hydrogen bonding interactions [22]. The bond at 3551 and 3523 cm⁻¹ are due to the N-H asymmetric stretching and symmetric stretching vibrations respectively [23]. The bonds at 3468, 3419 cm⁻¹ were assigned to the asymmetric and symmetric NH₂ stretching vibrations of the amine group respectively [24].

The aromatic C-H stretching vibration appears at 3370 cm⁻¹ [25].

The peaks around 1612, 1564 and 1466 cm⁻¹ are due to the C = C, C = N and C-C stretching modes of the aromatic rings [24] [25] [26].

The bonds at 1424 and 1390 cm⁻¹ are consistent with asymmetric and symmetric C-N stretching vibrations respectively [24].

The weak bands are located at 1104 and 853 cm⁻¹ are due to the ν (C-N_{aromatic}) and ν (C-H) modes [27].

A weak band that appears at 685 cm⁻¹ is attributed to the C-Cl bending vibration [24].

The peak above 350 cm⁻¹ is assigned to ν (Fe-Cl) [28] [29].

3.4. UV-Vis Spectrum

The obtained UV-Vis Spectrum for the compound $\text{FeCl}_4(\text{C}_5\text{N}_2\text{H}_6)(\text{C}_5\text{N}_2\text{H}_5)$ hydrate in methanol was recorded at diluted concentration (5 × 10⁻⁴). The UV-Vis Spectrum reveals an absorption band at 358 nm (<400 nm) (**Figure 8**), indicates the π - π transitions into the ligands. Thus, the value of the experimental band-gap energy (E_g) estimated from the absorption edge wavelength is about 2.9 eV. This band-gap value confirms that the crystal exhibits semiconductor behaviour [30].



Figure 8. UV-Vis spectrum of the compound $\text{FeCl}_4(C_5N_2H_6)(C_5N_2H_5)$.

3.5. Thermal Analysis of FeCl₄(C₅N₂H₆)(C₅N₂H₅)

The TGA-DTA of $\text{FeCl}_4(C_5N_2H_6)(C_5N_2H_5)$ were performed on 10.9 mg under argon atmosphere, in the temperature range of 25°C - 470°C, at a heating rate of 10°C·min⁻¹ (**Figure 9**). The thermogram analysis for this compound shows that it degraded in three steps. First step represented that the percentage of the experimental mass loss is in the order of 1.329% (calculated 0.44%), in the temperature ranging from 80°C - 140°C, which the departure of H₂. This step is characterized by two endothermic peaks in a temperature range of 53°C - 100°C.



Figure 9. Thermal analysis of the title compound $\text{FeCl}_4(C_5N_2H_6)(C_5N_2H_5)$.

The second step involved a second loss mass corresponding to the decomposition of part of the organic base (NH and HCl) in the temperature ranging from 250°C - 325°C (experimental 11.528%, calculated 11.30%) [31] [32]. This stage is characterized by an endothermic peak at 298°C. In the final step, the TG trace shows an 8.372% loss in weight, which is calculated in the order of 10.02% in the range 330°C - 378°C, indicating the conversion to 1/2 FeCl [33]. This step is corresponded to an endothermic peak at 348°C.

4. Hirshfeld Surface Analysis

A Hirshfeld surface analysis and the associated 2D-fingerprint plots are the convenient way to investigate different types of intermolecular interactions and to dissect crystal structures into non-covalent contacts [34] [35] by the aid of Crystal Explorer program [36]. Figure 10(a) illustrates the Hirshfeld surface mapped over d_{norm} using different colours. Red areas highlight the closer contacts including the N-H…Cl hydrogen bonds. Blue areas represent longer contacts (no interactions) [26]-[37]. In the shape-index map (Figure 10(b)), the adjacent red and blue triangle show concave regions that confirm the presence of the π - π interaction.

The 2D fingerprint plot shows the different types of interaction that assure the structure cohesion (Figure 11). The Cl…H/H…Cl play a dominant role with a significant contribution of 68.4% and the Cl…Cl contacts contributed with an



Figure 10. View of the Hirshfeld surfaces for $FeCl_4(C_5N_2H_6)(C_5N_2H_5)$ mapped over (a) d_{norm} and (b) shape-index, displaying the intermolecular interactions.



Figure 11. Full two-dimensional fingerprint plots showing all interactions, Cl…H (68.4%), Cl…Cl (9.5%), N…H (6.5%), C…C (1.6%), C…N (1.4%) and C…H (0.9%).

equal minor percentage at 9.5%. The contact N...H/H...N appears as a symmetrical tip shape with 6.5% of the total surface Hirshfeld area. Furthermore, the C...C contact contributed to the 2D fingerprint with an equal minor percentage at 1.6% confirms the presence of π - π interactions between the rings of 3-amino-2-chloropyridinium cations.

5. Conclusion

Red crystals of the new iron complex $\text{FeCl}_4(C_5N_2H_6)(C_5N_2H_5)$ were successfully synthesized by slow evaporation at room temperature. This compound crystallizes in the monoclinic system with the P2₁/c space group and is solved through single crystal X-ray diffraction. The PXRD confirms a high purity of the synthesized sample. The IR Spectroscopy technique was used to identify the vibrational absorption bonds of the crystal structure. Thus, the optical properties were performed by measuring the diffuse reflectance and the band-gap energy (E_g) of this compound was found to be at 2.9 eV. The results of thermal analysis TGA-DTA were obtained to prove the thermal stability of the complex. The cohesion and the stability result from the establishment of hydrogen-bonding network consisting of N-H···Cl and π - π interactions between rings. Moreover, The Hirshfeld surface and fingerprints plots analysis showed the existence of intermolecular interactions in which N-H···Cl is the most abundant in this crystal structure.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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