

Synthesis, Characterization, and Crystal Structure Determination of Iron(III) Hetero-ligand Complex Containing Chloride, Dimethyl sulfoxide, pyridine-2, 6-dicarboxylate and Water, [Fe(Pydc)(DMSO)(H₂O)Cl]

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ABSTRACT

A new metal-organic compound, [Fe(Pydc)(DMSO)(H₂O)Cl], (where Pydc is pyridine-2, 6-dicarboxylate and DMSO is dimethyl sulfoxide), has been synthesized and characterized by single crystal X-ray diffraction, TGA/DTA, IR and Raman spectroscopy. Green-yellow crystals, crystallized in the monoclinic system, space group P2₁/n, a = 7.2461(4) Å, b = 10.3018(4) Å, c = 17.7667(10) Å, α = 90°, β = 90.014°(5), 1329.54(12) Å³, Z = 4 and R = 0.0317. In the molecule of the crystallized compound Fe ion is sixfold coordinated with distorted octahedral geometry and the structure is stabilized by O-H...O hydrogen bonds.

Keywords: Crystal structure, metal-organic structure, FeIII complex, pyridine ring, hydrogen bond

INTRODUCTION

The design and synthesis of metal-organic compounds have received extensive interest due to their intriguing structural topologies as well as a potential application as functional materials. Complexes of the pydc, benzenetetracarboxylate and a few other carboxylates ligand with a mono-, bi- and trivalent lanthanide and transition metals have been investigated, synthesized and characterized by different researchers [1-4]. In these complexes, pydc acts as an N- and O-atom donor ligand, forming coordination polymers in the solid state. The titled compound [Fe(Pydc)(DMSO)(H₂O)Cl]

structure was reported in 2006 [5]. In this research compound **1** has been characterized using single crystal X-ray diffraction, powder X-

ray diffraction, DTA-TGA, IR and Raman spectroscopy.

EXPERIMENTAL

2.1. Materials and methods

All chemicals purchased were of reagent grade without further purification. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was performed on a Netzsch STA 409, thermogravimetric analyzer under atmospheric environment at a heating rate of 10°C/min. The infrared spectrum was recorded within the 400-4000cm⁻¹ region on a Bruker FT-IR spectrometer using KBr pellets. Raman spectra of the samples were collected using Thermo Nicolet Almega

dispersive micro-Raman scattering spectrometer operating by a 532 nm laser line in a back-scattering configuration with a laser power of about 30 mW with the spectral resolution of 4 cm^{-1} . The powder X-ray pattern of compound 1 investigated using Philips X-pert pro instrument.

2.2. Synthesis

The H_2pydc solution (0.7 g, 4.2 mmol) was dissolved in 20 ml of DMSO solution, and 1.135 gr (4.2 mmol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 ml of water. The first solution was added to aqueous solution with gentle stirring and refluxed for 5h in 70°C . The consequent pale-yellow solution evaporated at room temperature up to reaching to gel state. The consequent gel was dissolved in 20 ml of acetonitrile and left at room temperature for 6 months, forming green-yellow prismatic crystals (70.2%) with melting point of 216°C .

2.3. X-ray crystal structure determination

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-K_α radiation. For $[\text{Fe}(\text{Pydc})(\text{DMSO})(\text{H}_2\text{O})\text{Cl}]$, a green-yellow prismatic crystal with a dimension of $0.60 \times 0.45 \times 0.31\text{ mm}$ was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 4048 unique reflections. Data were collected at a temperature of $293(2)\text{ K}$ to a maximum 2θ value of 61.08° and in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [I] software package. The numerical absorption coefficients, μ , for Mo-K_α radiation are 1.512 mm^{-1} . A numerical absorption correction was applied using X-RED [II] and X-SHAPE [III] software's. The data were corrected for Lorentz

and Polarizing effects. The structures were solved by direct methods [IV] and subsequent difference Fourier map and then refined on F^2 by

a full-matrix least-squares procedure using anisotropic displacement parameters [IV].

All of hydrogen atoms were located in a difference Fourier map and then after refined isotropically.

Subsequent refinement then converged with R factors and parameters errors significantly better than for all attempts to model the solvent disorder. Atomic factors are from International Tables for X-ray Crystallography [V]. All refinements were performed using the X-STEP32 crystallographic software package [VI].

I. Stoe & Cie, X-Area, version 1.30: Program for the acquisition and analysis of data; Stoe & Cie GmbH: Darmstadt, Germany (2005).

II. Stoe & Cie, X-RED, version 1.28b: Program for data reduction and absorption correction; Stoe & Cie GmbH: Darmstadt, Germany (2005).

III. Stoe & Cie, X-SHAPE, version 2.05: Program for crystal optimization for numerical absorption correction; Stoe & Cie GmbH: Darmstadt, Germany (2004).

IV. G. M. Sheldrick, (1997), SHELX97. Program for crystal structure solution and refinement. University of Göttingen, Germany.

V. International Tables for X-ray Crystallography, Vol C, Kluwer Academic Publisher, Dordrecht, The Netherlands (1995).

VI. Stoe & Cie, X-STEP32, Version 1.07b: Crystallographic package; Stoe & Cie GmbH: Darmstadt, Germany (2000).

Crystallography data, atomic coordinate, bond lengths and angles, anisotropic displacement parameters, Hydrogen coordinates and torsion angles are presented in Tables 1 to 6 respectively.

Table1. Crystal data for [Fe(Pydc)(DMSO)(H₂O)Cl]

| | |
|--|---|
| Empirical formula | C ₉ H ₁₁ ClFeNO ₆ S |
| Formula weight | 352.55 |
| Temperature | 293(2) K |
| Wavelength (λ Mo K α) | 0.71073 Å |
| Crystal system, space group | Monoclinic, P2 ₁ /n |
| Unit cell dimensions | a= 7.2461 (4) Å α = 90° b= 10.3018 (4) Å β = 90.014(5)° c= 17.7667 (10) Å γ = 90° |
| Volume | 1329.54 (12) Å ³ |
| Z, calculated density | 4, 1.761 Mg m ⁻³ |
| Absorption coefficient | 1.512 mm ⁻¹ |
| F(000) | 716 |
| Crystal size | 0.60 x 0.45 x 0.31 mm ³ |
| Theta range for data collection | 2.29 to 30.54° |
| Limiting indices | -10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25 |
| Reflection collected / unique | 27972 / 4048 (R _{int} = 0.0436) |
| Completeness to theta = 30.54 | 99.6% |
| Absorption correction | Numerical |
| Max. and min. transmission | 0.7315 and 0.5536 |
| Refinement method | Full-matrix least-square on F ² |
| Data / restraints / parameters | 4048 / 0 / 180 |
| Goodness-of-fit on F ² | 1.037 |
| Final R indices [I > 2σ(I)] | R ₁ = 0.0317, wR ₂ = 0.0795 |
| R indices (all data) | R ₁ = 0.0389, wR ₂ = 0.0826 |
| Large diff. peak and hole | 0.328 and -0.431 eÅ ⁻³ |

Table 2. Selected geometric parameters (Å, °)

| | | | |
|-----------|-------------|------------|-------------|
| Fe1-O5 | 2.0140 (14) | Fe1-O1 | 2.0497 (12) |
| Fe1-O3 | 2.0203 (12) | Fe1-N1 | 2.0746 (13) |
| Fe1-O6 | 2.0427 (14) | Fe1-Cl1 | 2.2669 (5) |
| O5-Fe1-O3 | 92.17 (5) | O6-Fe1-N1 | 88.09 (6) |
| O5-Fe1-O6 | 174.66 (6) | O1-Fe1-N1 | 75.30 (5) |
| O3-Fe1-O6 | 91.86 (6) | O5-Fe1-Cl1 | 91.52 (5) |
| O5-Fe1-O1 | 88.39 (6) | O3-Fe1-Cl1 | 102.70 (4) |
| O3-Fe1-O1 | 151.27 (5) | O6-Fe1-Cl1 | 91.01 (5) |
| O6-Fe1-O1 | 86.40 (6) | O1-Fe1-Cl1 | 106.01 (4) |
| O5-Fe1-N1 | 89.48 (6) | N1-Fe1-Cl1 | 178.37 (4) |
| O3-Fe1-N1 | 75.98 (5) | O5-S1-C8 | 103.92 (10) |
| S1-O5-Fe1 | 118.91 (8) | O5-S1-C9 | 102.74 (10) |
| C8-S1-C9 | 100.44 (14) | | |

Table3. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³). U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | X | Y | Z | Ueq |
|-------|---------|---------|---------|-------|
| Fe(1) | 6449(1) | 2577(1) | 1491(1) | 30(1) |
| Cl(1) | 8073(1) | 1724(1) | 520(1) | 53(1) |
| C(1) | 5579(3) | 5286(2) | 1779(1) | 34(1) |
| C(2) | 4750(2) | 4596(2) | 2451(1) | 32(1) |
| C(3) | 3827(3) | 5120(2) | 3062(1) | 38(1) |
| C(4) | 3159(3) | 4280(2) | 3602(1) | 44(1) |
| C(5) | 3439(3) | 2943(2) | 3541(1) | 39(1) |
| C(6) | 4406(2) | 2502(2) | 2923(1) | 31(1) |
| C(7) | 4974(2) | 1126(2) | 2742(1) | 31(1) |
| C(8) | 1985(4) | 4023(3) | 186(2) | 63(1) |
| C(9) | 2945(4) | 1672(2) | -406(1) | 59(1) |
| N(1) | 4999(2) | 3321(1) | 2400(1) | 31(1) |
| O(1) | 6315(2) | 4535(1) | 1293(1) | 38(1) |
| O(2) | 5512(2) | 6480(1) | 1729(1) | 46(1) |
| O(3) | 5913(2) | 1005(1) | 2134(1) | 35(1) |
| O(4) | 4546(2) | 235(1) | 3170(1) | 42(1) |
| O(5) | 4067(2) | 2381(1) | 922(1) | 44(1) |
| O(6) | 8820(2) | 2958(1) | 2068(1) | 41(1) |
| S(1) | 3912(1) | 2969(1) | 125(1) | 40(1) |

Table4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Fe. The anisotropic displacement factor exponent takes the form: $-2\pi_2(h_2a_2^*U_{11} + \dots + 2h_1k_1a_1^*b^*U_{12})$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|-------|-------|-------|-------|--------|--------|--------|
| Fe(1) | 38(1) | 26(1) | 27(1) | -1(1) | 2(1) | -2(1) |
| Cl(1) | 57(1) | 61(1) | 42(1) | -16(1) | 14(1) | 0(1) |
| C(1) | 44(1) | 28(1) | 32(1) | 3(1) | -7(1) | 0(1) |
| C(2) | 39(1) | 26(1) | 31(1) | 1(1) | -4(1) | 2(1) |
| C(3) | 45(1) | 30(1) | 39(1) | -5(1) | 0(1) | 5(1) |
| C(4) | 51(1) | 43(1) | 38(1) | -8(1) | 9(1) | 5(1) |
| C(5) | 46(1) | 39(1) | 32(1) | 2(1) | 6(1) | 0(1) |
| C(6) | 36(1) | 28(1) | 29(1) | 1(1) | -1(1) | 0(1) |
| C(7) | 34(1) | 26(1) | 33(1) | 1(1) | -2(1) | 0(1) |
| C(8) | 64(2) | 59(1) | 65(1) | 18(1) | 9(1) | 14(1) |
| C(9) | 76(2) | 59(1) | 43(1) | -3(1) | -9(1) | -15(1) |
| N(1) | 39(1) | 25(1) | 28(1) | 1(1) | 1(1) | 1(1) |
| O(1) | 51(1) | 31(1) | 31(1) | 4(1) | 3(1) | -1(1) |
| O(2) | 71(1) | 26(1) | 42(1) | 5(1) | -8(1) | 0(1) |
| O(3) | 44(1) | 25(1) | 36(1) | 0(1) | 5(1) | 1(1) |
| O(4) | 51(1) | 30(1) | 45(1) | 10(1) | 8(1) | 3(1) |
| O(5) | 43(1) | 53(1) | 34(1) | 9(1) | -5(1) | -10(1) |
| O(6) | 48(1) | 29(1) | 47(1) | 6(1) | -12(1) | -8(1) |
| S(1) | 41(1) | 45(1) | 35(1) | 6(1) | -2(1) | -7(1) |

Table5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Fe.

| | X | Y | Z | Ueq |
|-------|----------|----------|----------|----------|
| H(3A) | 3664 | 6012 | 3107 | 3107 |
| H(4A) | 2514 | 4609 | 4012 | 4012 |
| H(5A) | 2990 | 2372 | 3903 | 3903 |
| H(8A) | 1599 | 4268 | -311 | -311 |
| H(8B) | 2319 | 4786 | 465 | 465 |
| H(8C) | 994 | 3586 | 438 | 438 |
| H(9A) | 1921 | 1310 | -136 | -136 |
| H(9B) | 3860 | 1014 | -483 | -483 |
| H(9C) | 2532 | 1994 | -884 | -884 |
| H(61) | 9000(40) | 2570(30) | 2420(18) | 2420(18) |
| H(62) | 9270(40) | 3590(30) | 2023(15) | 2023(15) |

Table6. Torsion angles [$^\circ$] for Fe.

| | | | |
|-----------------------|------------|-----------------------|-------------|
| O(5)-Fe(1)-N(1)-C(6) | 90.90(13) | Cl(1)-Fe(1)-O(1)-C(1) | -175.26(12) |
| O(3)-Fe(1)-N(1)-C(6) | -1.46(12) | O(4)-C(7)-O(3)-Fe(1) | 178.91(14) |
| O(6)-Fe(1)-N(1)-C(6) | -93.86(13) | C(6)-C(7)-O(3)-Fe(1) | -1.87(19) |
| O(1)-Fe(1)-N(1)-C(6) | 179.37(14) | O(5)-Fe(1)-O(3)-C(7) | -87.10(13) |
| Cl(1)-Fe(1)-N(1)-C(6) | -37.2(16) | O(6)-Fe(1)-O(3)-C(7) | 89.40(13) |
| O(5)-Fe(1)-N(1)-C(2) | -91.39(13) | O(1)-Fe(1)-O(3)-C(7) | 3.5(2) |
| O(3)-Fe(1)-N(1)-C(2) | 176.25(14) | N(1)-Fe(1)-O(3)-C(7) | 1.83(12) |
| O(6)-Fe(1)-N(1)-C(2) | 83.85(13) | Cl(1)-Fe(1)-O(3)-C(7) | -179.15(12) |
| O(1)-Fe(1)-N(1)-C(2) | -2.92(13) | O(3)-Fe(1)-O(5)-S(1) | -156.26(10) |
| Cl(1)-Fe(1)-N(1)-C(2) | 140.6(15) | O(6)-Fe(1)-O(5)-S(1) | 64.8(7) |
| O(2)-C(1)-O(1)-Fe(1) | 176.35(15) | O(1)-Fe(1)-O(5)-S(1) | 52.48(10) |
| C(2)-C(1)-O(1)-Fe(1) | -3.9(2) | N(1)-Fe(1)-O(5)-S(1) | 127.79(10) |
| O(5)-Fe(1)-O(1)-C(1) | 93.62(14) | Cl(1)-Fe(1)-O(5)-S(1) | -53.49(9) |
| O(3)-Fe(1)-O(1)-C(1) | 2.1(2) | Fe(1)-O(5)-S(1)-C(8) | -123.47(13) |
| O(6)-Fe(1)-O(1)-C(1) | -85.24(14) | Fe(1)-O(5)-S(1)-C(9) | 132.21(12) |
| N(1)-Fe(1)-O(1)-C(1) | 3.73(13) | | |

RESULTS AND DISCUSSION

3.1. Structure description

The metal coordination environments of title compound **1** are shown in Fig. 1. The coordination of the Fe atom in (I) is a distorted octahedral. The site occupied by O atoms of the pydc ligand show a distortion in the equatorial plane. The O1-Fe1-O3 angle is distorted from linearity by about 28.73°. The angle of S1-O5-Fe1 is 118.91(8). These observed large angles may belong to the steric hinderances induced by methyl groups of DMSO and lone pairs on oxygen of DMSO with Fe atom environment. According to experimental geometry data for DMSO-bond angles are: CSC: 96.5° and CSO: 106.5°. At this complex the bond angles of DMSO ligand are: e.g. C8-S1-C9: 100.44(4)°; O5-S1-C9: 102.74(10)° and for O5-S1-C18: 103.92(10)°. Therefore they almost have not been changed. The other four sites around the Fe atoms are occupied by two O atoms of dimethyl sulfoxide and water molecules in vertical direction, one N atom of the pydc ligand and one Cl atom in equatorial direction, producing a square skeleton with slightly distortion to tetracarboxylate section. The Fe-Cl, Fe-N as well as Fe-O bond lengths are in agreement with the corresponding ones in $[\text{Fe}_2(\text{pydc})_2(\text{H}_2\text{O})_6].2\text{pydcH}_2$ [3]. The crystal structure is stabilized by intermolecular O-H...O hydrogen bonds, where linking the molecules in chains.

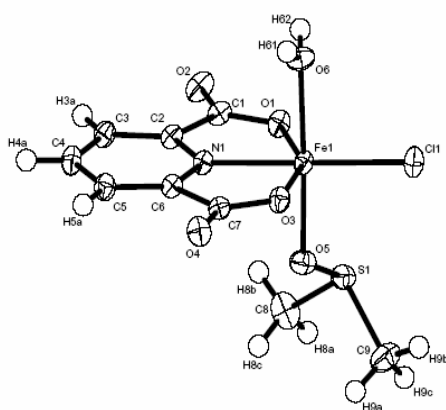


Fig.1. The molecular structure of **1** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability.

3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves have been obtained in air for titled compound in the temperature range of 35-1000°C (Fig. 2). The TGA curve exhibit four well-separated weight loss stages in the temperature ranges of 184.2°C to 220°C with 7.36% weight loss, 220°C to 300°C with 28.98% weight loss, 300°C to 450°C with 16.10 weight loss and 450°C to 640°C with 28.10 weight loss. From this point a black stable phase Fe_2O_3 remain constant, indicating an 80.06% weight loss.

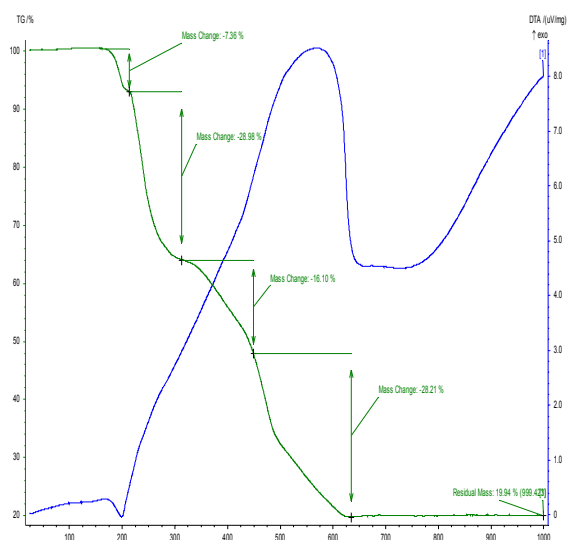


Fig.2. DTA/TGA curves of **1** recorded in air.

3.3. Raman Spectroscopy

Typical recorded Raman spectra of the sample have been illustrated in Fig. 3. In the Raman spectra four distinct regions can be clearly distinguished.

Region a: The high frequency region which is mainly in the spectral region of 2800-3100 cm^{-1} and are assigned as the C-H symmetric and asymmetric stretching vibrational modes.

Region b: The medium frequency region located in the spectral region of 1400-1700 cm^{-1} corresponding to C-C and C=O modes.

Region c: This region, which is located in the 400-1400 cm^{-1} , is assigned as the internal lattice modes of the compound such as the internal modes of the Fe-Cl, Fe-N and Fe-O bonds.

Region d: The low wavenumber region in the Raman spectral region below 400 cm^{-1} has been assigned as the external lattice modes of the structure mainly due to external lattice vibrations, librations and backbone deformations.

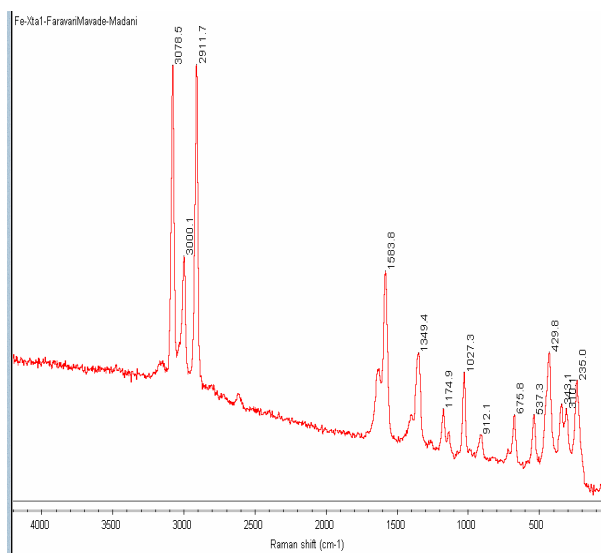


Fig.3. Raman spectra of compound 1.

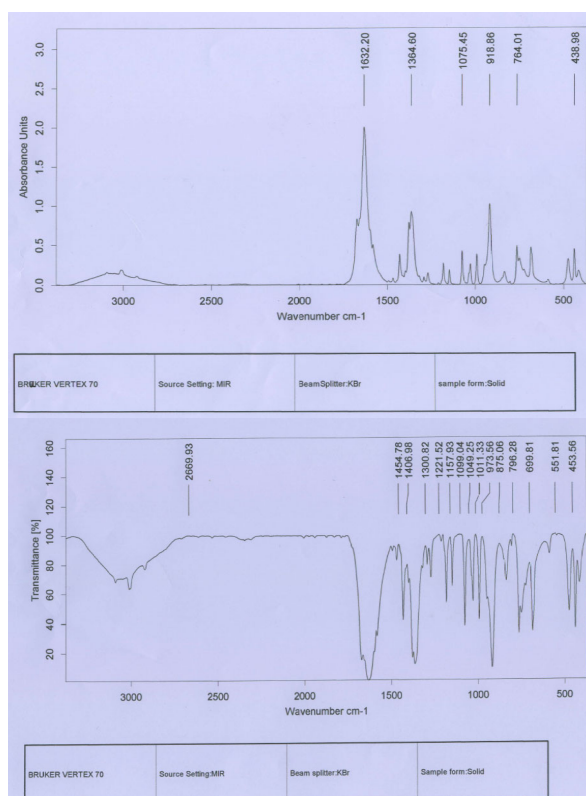


Fig.4. IR spectrum of compound 1.

3.4. FT-IR spectroscopy

The IR spectrum of compound 1 (Fig. 4) shows the characteristics bands in 2900 to 3300 cm^{-1} which is attributed to the vibration of O-H of water molecule coordinated with iron [8]. The absorbance band at about 1633 cm^{-1} and of 363 cm^{-1} are assigned to $\nu(\text{S}=\text{O})$ and Fe-O(DMSO) correspondently [9].

The absorbance band at 389 cm^{-1} is attributed to $\nu(\text{Fe}-\text{OH}_2)$ and $\text{Pw}(\text{H}_2\text{O})=575 \text{cm}^{-1}$ [9] and bands of 1292 cm^{-1} , 1429 cm^{-1} and 1620 cm^{-1} are assigned to $\nu \text{C}-\text{O}$ [8], $\nu_{\text{sym}}\text{COO}$ and $\nu_{\text{asym}}\text{COO}$ respectively [9]. Absorbance band of $\text{C}=\text{N}$ pyridine's ring appears in 1590 cm^{-1} .

In the literature absorbance bands of 260 cm^{-1} attributed to vibration of Fe-N [11], while those of 286 cm^{-1} and 299 cm^{-1} related to Fe-Cl vibration [12-13]. Absorbance band of 440 cm^{-1} and 681 assigned to deformational modes of pyridine's ring as well as to M-O bands [9a&9b].

3.5. Powder X-ray pattern

The sample were powdered by mortar and pestle and prepared on zero background Si-cut sample holder. The powder X-ray pattern of compound 1 investigated using Philips x-pert pro instrument. The diffractogram and table of lines, and intensity presented in Table (7) and Fig. (5).

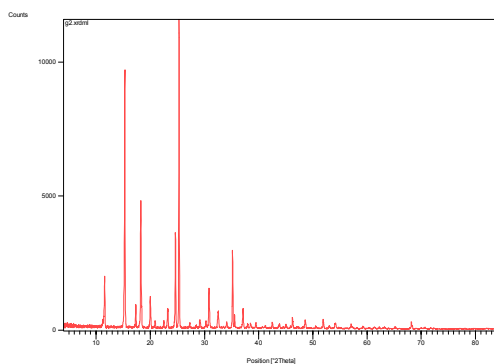


Fig.5. Diffractogram of compound 1.

CONCLUSION

In summary, we have successfully synthesized and characterized a new metal-organic molecule of aquachloro (dimethyl sulfoxide-kO) (pyridine-2, 6-dicarboxylato-k3O,N,O')iron(III), in which pydc acts as an N- and O-atoms donor ligand, forming coordination polymers in solid state.

Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center with the deposition No. of CCDC.

Copies of this data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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REFERENCES

1. M.G.B. Drew, R.W. Mathews, R.A. Walton, *J. Chem. Soc.* (1970) 1405.
2. M.B. Cingi, A.C. Villa, C. Guastini, M. Nardelli, *Gazz.Chim. Ital.* 102 (1972) 1026.
3. P.Laine, A. Gourdon, J.P. Launay, J.P. Tuchagues, *Inorg. Chem.*, 34 (1995) 5150.
4. M.Rafizadeh, M. Ranjbar, V. Amani, *Acta Cryst. E*60 (2004) m749.
5. M.Rafizadeh, B. Mehrabi, V. Amani, *Acta Cryst. E*62 (2006) m1332.
6. Stoe & Cie, XAREA (Version 1.31) and X-RED32 (Version 1.26), (2005), Stoe & Cie.
7. G.M. Sheldrick, SHELX97 and SHELXL97, (2005), University of Gottingen.
8. S.C. Mojumdar, I. Onderjkovicova, L. Nevidanska, M. Melink, *J. Anal. Appl. Pyroly.* 64, (2002), 59.
9. K.Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compound, Part B.* (1997) John Wiley.
10. L.Yu-Cang, H. Mao-Chun, C. Rong, W. Jia-Bao, *Chinese J. Struct. Chem.* 20,6, (2000) 455.
11. Y.Kidani, M. Noji, H. Koike, *Bull. Chem. Soc. Japan*, 48 (1975) 239.
12. Y.Saito, J. Takemoto, B. Hutchinson, K. Nakamoto, *Inorg. Chem.* 11,9, (1972), 2003.
13. W.M. Reiff, B. Docum, M.A. Webber, R.B.Trankel, *Inorg. Chem.* 14, 4, (1975) 800.
14. O.V.Quintani, S. Tarutti, O.E. Piro, E. J. Baran, E. E. Castellano, *Z. Natu. Porsch.* %2b, (1997) 183.