

Synthesis, Characterization and Crystal Structure of Caffeine Complex of Mn(II) *p*-Hydroxybenzoate

Öztürkkan Özbek, Füreya Elif*⁺; Sertçelik, Mustafa

Department of Chemical Engineering, Faculty of Engineering and Architecture, Kafkas University, 36100 Kars, TURKEY

Taşdemir, Erdal

Department of Chemistry, Faculty of Sciences and Arts, Kafkas University, 36100 Kars, TURKEY

Hökelek, Tuncer

Department of Physics, Hacettepe University, 06800 Beytepe, Ankara, TURKEY

Çatak Çelik, Raziye

Scientific and Technological Application and Research Center, Aksaray University, 68100 Aksaray, TURKEY

Necefoğlu, Hacali*

Department of Chemistry, Faculty of Sciences and Arts, Kafkas University, 36100 Kars, TURKEY

ABSTRACT: A new manganese(II) complex containing *p*-hydroxybenzoate and caffeine ligands, namely $[Mn(OH-C_6H_4COO)_2(H_2O)_4] \cdot 2(C_8H_{10}N_4O_2) \cdot 8H_2O$ has been prepared. The synthesized complex has been characterized by elemental analyses, FT-IR spectroscopy, X-ray crystallography, and molar conductance measurements. The thermal properties of the complex were analyzed by TGA/DTA. The complex crystallizes in the monoclinic space group $P2_1/c$ having cell dimensions $a=11.1311(2)$, $b=14.3579(3)$, $c=13.5383(3)$ Å, $\beta=101.879(2)^\circ$, $V=2117.34(8)$ Å³, $Z=2$. In the mononuclear complex, Mn atom is coordinated by two *p*-hydroxybenzoate anions and four water molecules. Moreover, the asymmetric unit of the complex also contains four uncoordinated water molecules and one caffeine ligand. Crystal structure of the complex have 3D supramolecular networks formed via $O-H_{OH} \cdots O_{caf}$, $O-H_w \cdots O_w$, $O-H_w \cdots N_{caf}$, $O-H_w \cdots O_{caf}$ and $O-H_w \cdots O_{car}$ hydrogen bonds.

KEYWORDS: Mn(II); Caffeine; *p*-hydroxybenzoic acid; Supramolecular crystal structure.

INTRODUCTION

In recent years, the syntheses of the complexes which have supramolecular structure and determination of their

structures have attracted both coordination chemists' and materials scientists' attention. As well as the structure

* To whom correspondence should be addressed.

+ E-mail: fozturkkan36@gmail.com

• Other Address: International Scientific Research Centre, Baku State University, 1148 Baku, AZERBAIJAN
1021-9986/2019/6/251-259 9/\$/5.09

properties of complexes with supramolecular structures they have a wide area of use with their gas storage, optical and magnetic properties [1-4]. A number of supramolecular metal complexes of ligands containing nitrogen, oxygen and sulphur donor atom take part in literature. The coordination geometry of metal centre as much as the structure of ligands plays an important role in the formation of these structures [5, 6]. The structure architecture of manganese complexes have attracted great interest in recent years, owing to their design and construction of structures and potential applications in the fields of antibacterial, anticancer, antifungal, other biologically properties and catalytic activities [7-14]. There are manganese *p*-hydroxybenzoate complexes in the literature which have octohydrate and trihydrate coordination with $[\text{Mn}(\text{H}_2\text{O})_6](p\text{-HOC}_6\text{H}_4\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Mn}(\text{H}_2\text{O})_2(p\text{-HOC}_6\text{H}_4\text{COO})_2] \cdot \text{H}_2\text{O}$ general formula [15]. The complexes of *p*-hydroxybenzoic acid with manganese and 1,10-phenanthroline and 2,2'-bipyridine which have $[\text{Mn}(\text{C}_7\text{H}_5\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})](\text{C}_7\text{H}_5\text{O}_3)$ and $[\text{Mn}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ general formula and complexes with octohedral coordination were synthesized by various research groups [16, 17]. A number of complexes of Mn(II) with various donor atoms in its complexes with benzoates [18-22]. In our previous work, we synthesized caffeine adducts of Co(II), Ni(II) and Zn(II) *p*-hydroxybenzoates and characterized their crystal structures [23]. In this study, we synthesized Mn(II) *p*-hydroxybenzoate caffeine complex which has supramolecular structure, and we illuminated its structure through elemental analysis, FT-IR spectroscopy and X-ray diffraction. We also studied the thermal behaviours of complexes through TGA/DTA.

EXPERIMENTAL SECTION

Material and instruments

Analytical grade reagents were used throughout this work without any further purification. Elemental analysis for C, H and N were performed on a LECO, CHNS-932 elemental analyzer. FT-IR Spectra were recorded on Perkin Elmer Frontier™ FT-IR Spectrometer with solid samples using a Diamond ATR accessory in the range of 4000-600 cm^{-1} . Resolution was set up to 4 cm^{-1} , signal/noise ratio was established by 4 scans. The thermal properties of the complexes were performed and recorded simultaneously in a static nitrogen atmosphere with

a help of Shimadzu DTG 60 thermal analyzer. The experiments were performed in static nitrogen with a heating rate of 10 $^\circ\text{C min}^{-1}$ from room temperature to 1000 $^\circ\text{C}$ in platinum crucibles. The samples were approximately 10 mg and highly sintered $\alpha\text{-Al}_2\text{O}_3$ was used as a reference material. The DTG sensitivity was 0.05 mg/s. Molar conductivity of the complexes were measured by using COND iSET315 in DMF (10^{-3} M) at room temperature.

X-ray crystallography

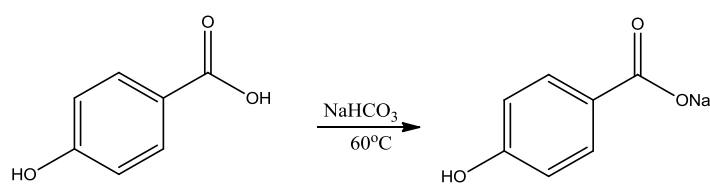
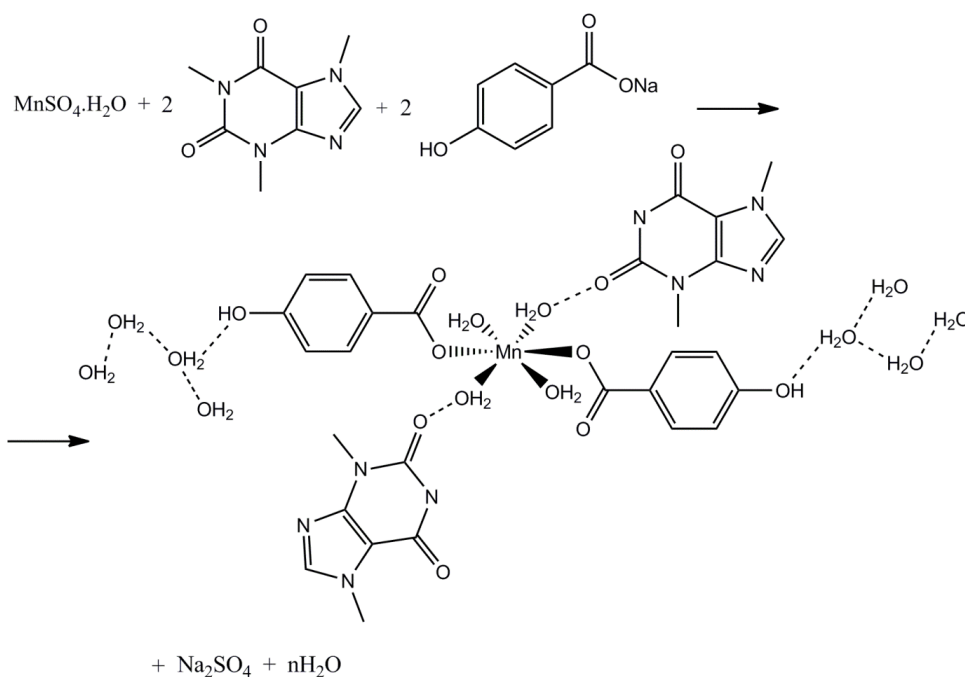
Single-crystal X-ray diffraction analysis of **1** was performed on a Bruker SMART BREEZE CCD diffractometer using Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at a temperature of 296 K. Structure was solved by direct methods [24] and refined by full-matrix least squares against F^2 using all data. All non-H atoms were refined anisotropically. Atoms H41, H42, H51, H52, H81, H82, H91, H92, H101, H102, H111 and H112 (for H_2O) was located in a difference Fourier map and refined isotropically, while the O- and C-bound H atoms were positioned geometrically at distances of 0.82 Å (OH) and 0.96 Å (for CH_3) from the parent O and C atoms; a riding model was used during the refinement processes and the U_{iso} (H) values were constrained to be $1.5U_{\text{eq}}$ (carrier atom). Experimental data are given in Table 1. CCDC: **1478281**.

Synthesis of the Complex

Firstly, 2 mmol of *p*-hydroxybenzoic acid was added to a water solution of 2 mmol NaHCO_3 (200 mL) and stirred at 60 $^\circ\text{C}$ temperature till removed of CO_2 gas to prepared the sodium *p*-hydroxybenzoate solution. The reaction scheme related to synthesis of sodium *p*-hydroxybenzoate was given as follow:

2 mmol caffeine (200 mL) was added to 100 mL of 1 mmol manganese sulfate solutions. The prepared sodium *p*-hydroxybenzoate solution was added to this solution (MnSO_4 + caffeine). After two weeks, the obtained colorless products were filtered off, washed with distilled water and dried in air atmosphere. The obtained all crystals were suitable for single crystal X-ray analysis. The reaction was given in following reaction scheme:

Anal. Calcd. (%): $\text{C}_{30}\text{H}_{54}\text{MnN}_8\text{O}_{22}$: C, 38.59; H, 5.83; N, 12.00, Found. (%): C, 38.41; H, 6.10; N, 12.03; Selected IR bands (cm^{-1}): $\nu(\text{OH})_{\text{H}_2\text{O}}$ 3374, $\nu(\text{OH})_{\text{phen}}$.

Scheme 1: Synthesis of the sodium *p*-hydroxybenzoate.

Scheme 2: Synthesis of the complex.

3262, $\nu(\text{C-H})_{\text{arom}}$. 3118, $\nu(\text{C-H})_{\text{CH}_3}$. 2957, $\nu(\text{C=O})_{\text{caff}}$. 1689, $\nu(\text{C=N})_{\text{caff}}$. 1637, $\nu(\text{COO}^-)_{\text{as}}$ 1599, $\nu(\text{COO}^-)_{\text{s}}$ 1388, $\Delta\nu(\text{COO}^-)$ 201, $\nu(\text{C-C})_{\text{phen}}$ 1465, $\nu(\text{C-OH})_{\text{phen}}$. 1236, $\delta(\text{COO}^-)$ 861, $\delta(\text{C-H})_{\text{phen}}$. 743, $\rho_r(\text{H}_2\text{O})$, 788 $\rho_w(\text{H}_2\text{O})$ 622. Molar Conductivity: 7.7 $\mu\text{S/cm}$.

RESULT AND DISCUSSION

The complex prepared is stable at room temperature. It is insoluble in solvents such as CCl_4 and CHCl_3 , weak soluble in EtOH and MeOH and soluble in $(\text{CH}_3)_2\text{CO}$, DMSO, DMF and H_2O .

Descriptions of the crystal structures

The result of X-ray structural analysis and the spectroscopic data of the synthesized complex are assignment. In Table 2, some of the bond lengths

and angles are shown. H-bond geometry is given in Table 3. The molecular structure scheme and the packing diagram are given in Figs. 1 and 2, respectively.

The mononuclear complex is isostructural with caffeine adducts of Co(II), Ni(II) and Zn(II) *p*-hydroxybenzoates [23]. The metal atom, Mn1, is placed on an inversion centre, which is coordinated through two *p*-hydroxybenzoate (PHB) ligands and four water molecules. All ligands coordinating in a monodentate manner. The asymmetric unit includes four non-coordinated water molecules and one non-coordinated caffeine molecule (Fig. 1). The four symmetry-related oxygen atoms O4, O4i, O5 and O5i of water molecules create a slightly distorted square-planar arrangement. The slightly distorted octahedral coordination sphere is completed by the two symmetry-related oxygen atoms

Table 1: Experimental details for 1.

	1
Empirical Formula	C ₃₀ H ₅₄ MnN ₈ O ₂₂
Formula weight, Colour/shape	933.75 colourless/block
Crystal System	monoclinic
Space Group	P2 ₁ /c
a (Å)	11.1311(2)
b (Å)	14.3579(3)
c (Å)	13.5383(3)
β (°)	101.879(2)
V (Å ³)	2117.34(8)
Z	2
μ (Mo K _α) (mm ⁻¹)	0.403
ρ (calcd) (mg m ⁻³)	1.465
Number of Reflections Total	5245
Number of Reflections Unique	4679
R _{int}	0.0322
2θ _{max} (°)	56.66
T _{min} / T _{max}	0.8238 / 0.9129
Number of Parameters	328
GOF	1.068
R [F ² > 2σ(F ²)]	0.0488
wR	0.1398
(Δρ) _{max} (e Å ⁻³)	1.186
(Δρ) _{min} (e Å ⁻³)	-0.374

(O1 and O1i) of the two PHB anions in the axial positions [symmetry code: (i) 2 - x, 1 - y, 1 - z]. There are the intermolecular O-H...O hydrogen bonds (Table 3) between uncoordinated water molecules, the PHB anions and the caffeine ligands (Fig. 1).

The same C1-O1 and C1-O2 bond lengths (Table 2) of the PHB anions show delocalized bonding arrangements, rather than localized single and double bonds. The average Mn-O_w bond length is 2.2124(15) Å and Mn-O_{coo} 2.1441(14) Å. The Mn1 atom deviates 0.3931 (1) Å from the planar (O1/C1/O2) carboxylate group. The O-Mn-O bond angles are closely to ideal values, with average values of 90.00(6)° (Table 2). Carboxylate group (O1/C1/O2) and the adjacent benzene ring [A (C2-C7)] are almost coplanar

due to the dihedral angle between them is 0.51(20)°. The purine ring system D (N1-N4/C8-C12) is planar. N3 atom deviates 0.0215(19) Å from this plane. Caffeine ring is oriented with respect to the benzene ring at a dihedral angle of A/B = 1.70(5)°.

The molecules formed of the crystal structure are linked via intermolecular O-H_{OH}...O_{caf} (caf = caffeine), O-H_w...O_w (w = water), O-H_w...N_{caf}, O-H_w...O_{caf}, O-H_w...O_{OH} and O-H_w...O_{car} (car = carboxylate) hydrogen bonds (Table 3), resulting in a 3D supramolecular network (Fig.2). The π...π interactions between the benzene [A (C2-C7)] and caffeine [B (N1/N2/C8-C10) and C (N3/N4/C9-C12)] rings, Cg1... Cg2, Cg1... Cg2i, Cg3... Cg1 and Cg3... Cg1i [symmetry code: (i) x, ½ - y, z - ½, where Cg1, Cg2 and Cg3 are the centroids of the rings A (C2-C7), B (N1/N2/C8-C10) and C (N3/N4/C9-C12), respectively] may stabilize the structure with the centroid-centroid distances of 3.658(1) Å, 3.685(1) Å, 3.580(1) Å and 3.500(1) Å, respectively.

FT-IR Spectra

The FT-IR spectrum is given in the Supplementary Fig. 1. Broad O-H stretching vibrations in the region of 3500-3200 cm⁻¹ correspond to coordinated and lattice water molecules. The stretching frequencies of phenolic O-H and phenolic C-O are observed at ca. 3260 and 1230 cm⁻¹, respectively. The stretching frequency of phenolic C-OH of the *p*-hydroxybenzoic acid is showed around 1250 cm⁻¹ and this peak remained nearly in the same position in our synthesized complex [27]. According to the literature, the coordination modes of carboxylate groups of the benzoate ligands have been determined by calculating from a difference between ν_{as}(CO₂⁻) and ν_s(CO₂⁻) and this value has been described as Δν(CO₂⁻). In example, monodentate carboxylate groups's Δν(CO₂⁻) value show a difference higher than related carboxylic acid's sodium salt's Δν(CO₂⁻) value. For the present complex, Δν(CO₂⁻) value is 201 cm⁻¹ and this value is higher than Δν(CO₂⁻) of sodium *p*-hydroxybenzoate (131 cm⁻¹) [28]. The stretching vibration C-H of methyl groups of caffeine molecules are showed at 2957 cm⁻¹. The absorption bands of carbonyl ν(C=O) and ν(C=N) of caffeine are observed at 1689 and 1637 cm⁻¹. The ρ_r(H₂O) and ρ_w(H₂O) absorption bands related to the presence of coordinated water are appeared at 788 and 622 cm⁻¹, respectively [29, 30].

Table 2: Selected bond lengths (Å) and angles (°) for 1.

1	
Mn1-O1	2.144(14)
Mn1-O4	2.209(15)
Mn1-O5	2.216(16)
O1-C1	1.259(3)
O2-C1	1.259(3)
O3-C5	1.369(2)
O6-C11	1.241(2)
O7-C12	1.224(3)
O1-Mn1-O4	89.04(6)
O1-Mn1-O4 ⁱ	90.96(6)
O1-Mn1-O5	92.55(6)
O1-Mn1-O5 ⁱ	87.45(6)
O4-Mn1-O5	92.55(6)
O4-Mn1-O5 ⁱ	87.45(6)
O1-C1-O2	123.83(18)

Symmetry code: (i) 2 - x, 1 - y, 1 - z.

Table 3: Hydrogen-bond geometry for 1 (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
O3-H3A...O6 ⁱⁱ	0.82	1.94	2.760 (3)	177
O4-H41...O7	0.90(2)	1.92(2)	2.788 (3)	162(2)
O4-H42...O2 ⁱ	0.84(3)	1.84(3)	2.617 (2)	155(3)
O5-H51...O9 ⁱⁱⁱ	0.90(3)	1.93(3)	2.812 (3)	167(3)
O5-H52...N1 ^{iv}	0.84(3)	2.02(3)	2.850 (3)	169(3)
O8-H81...O2 ^v	0.94(3)	1.76(3)	2.697 (3)	175(4)
O8-H82...O9	0.83(3)	2.01(3)	2.838 (3)	171(3)
O9-H91...O10	0.97(2)	1.70(2)	2.669(3)	178(1)
O9-H92...O3	0.82(2)	2.06(3)	2.841(3)	159(4)
O10-H101...O4 ^{vi}	0.88(4)	2.00(3)	2.871(3)	167(5)
O10-H102...O11	0.80(3)	1.93(3)	2.709(4)	167(3)
O11-H111...O8 ^{vii}	0.83(3)	2.01(3)	2.835(4)	171(4)
O11-H112...O8 ^{viii}	0.92(3)	1.96(3)	2.869(3)	168(4)

Symmetry codes: [(i) -x+2, -y+1, -z+1; (ii) x, y-1, z; (iii) -x+1, y+1/2, -z+1/2; (iv) x+1, y, z; (v) x-1, y, z; (vi) -x+1, -y+1, -z+1; (vii) x, -y+1/2, z-1/2; (viii) -x, y+1/2, -z+1/2.

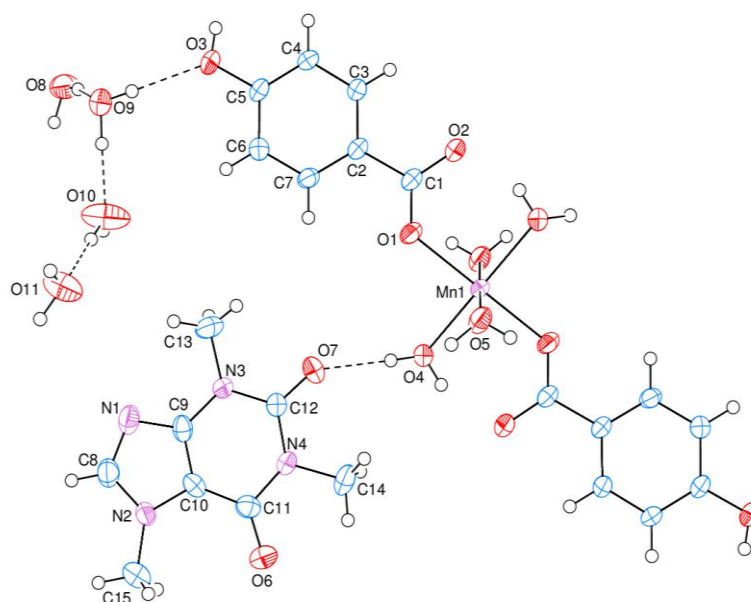


Fig. 1: An ORTEP-3 [25] view of 1. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

Thermal Analysis

TGA/DTA curves related to the complex has been given in Supplementary Fig. 2. Decomposition of complex consists of two general steps. The first one is dehydration process whereas takes place the loss of coordinated an uncoordinated water molecules. The second step is related with degradation of anhydrous complexes. Final product of thermal decomposition of complex is metal oxide. The TGA/DTA data of the complex show a weight loss of 21.99 % in the temperature range of 60–190°C attributed to the loss of four coordinated and eight lattice water molecules (Calcd. 23.17%). According to the literature, uncoordinated water molecules are removed at from 50-150°C and coordinated water molecules is removed over 150°C [32]. The loss of all water molecules in the complex is carried out at 190°C. After dehydration steps, the loss of two caffeine molecules occurs in a consecutive two steps in the temperature range of 180-400°C (Calcd.: 54.11 %; Found.: 53.51 %). MnO₂ is formed as the final solid product of the thermal decomposition of the complex (Calcd. 9.31 %; Found. 10.61 %) [31].

Molar conductivity

The molar conductance of the complex in DMF for $\approx 10^{-3}$ M solutions at room temperature is 7.7 $\mu\text{S}/\text{cm}$

and too small than 1:1 electrolyte type's value which indicates the non-electrolytic nature of the complex [32].

CONCLUSIONS

Supramolecular Mn(II) *p*-hydroxybenzoate with caffeine complex has been prepared and characterized. The IR studies showed that carboxylate groups of *p*-hydroxybenzoate ligands have monodentate coordination mode. The Mn²⁺ ion is octahedrally coordinated by two *p*-hydroxybenzoate ligands, four water molecules leading to an overall MO₆ coordination environment. The asymmetric unit of the mononuclear complex comprises one Mn(HO-C₆H₄COO)₂(H₂O)₄ moiety, one caffeine and four water molecules. The medium-strength hydrogen bondings involving the uncoordinated caffeine ligands and water molecules, coordinated and uncoordinated water molecules and *p*-hydroxybenzoate ligands lead to three-dimensional supramolecular networks in the crystal structure. One non-coordinating caffeine ligand and four water molecules are embedded, which are hydrogen bonded into chains. In the crystal structures of complexes, O-H_{OH}...O_{caf}, O-H_w...O_w, O-H_w...N_{caf}, O-H_w...O_{caf} and O-H_w...O_{car} hydrogen bonds link the molecules into three-dimensional supramolecular structure.

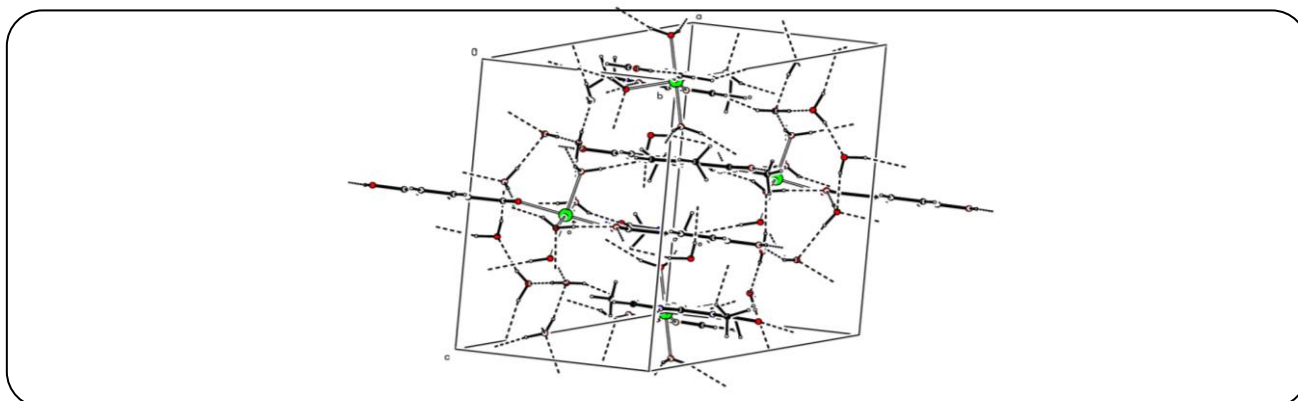


Fig. 2: A partial packing diagram of 1. Hydrogen bonds are shown as dashed lines [26].

Received : Jul. 20, 2018 ; Accepted : Oct. 14, 2018

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