

Synthesis spectroscopic characterization and X-ray crystal structure of heptacoordinated Mn(II) complex derived from NN'-15-bis (pyridylmethylidene)carbonohydrazone ligand

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Abstract

A new Mn(II) complex prepared by the reaction of NN'-15-bis (pyridylmethylidene) carbonohydrazone (H_2L) with Mn(II) ion is reported in this paper. The H_2L ligand is structurally characterized by elemental analysis NMR and infrared spectroscopies. The mononuclear complex $[Mn(H_2L)_2(H_2O)_2] \cdot (ClO_4)_2 \cdot 3(H_2O)$ is characterized by infrared spectroscopy conductance and magnetic room temperature measurements and single X-ray diffraction. The compound crystallizes in the triclinic system in the space group $P-1$ with the unit cell parameters $a = 10.8879(5) \text{ \AA}$ $b = 13.4705(6) \text{ \AA}$ $c = 15.3934(6) \text{ \AA}$ $\alpha = 100.846(4)^\circ$ $\beta = 101.676(4)^\circ$ $\gamma = 113.599(4)^\circ$ $Z = 2$ $R_1 = 0.0922$ and $wR_2 = 0.2538$ ($I > 2\sigma(I)$). The asymmetric unit of the compound contains a discrete $[Mn(H_2L)_2(H_2O)_2]^{2+}$ cation two free perchlorate anion and three uncoordinated water molecules. In the discrete cation one Mn^{2+} ion two organic ligand molecules and two coordinated water molecules are present. The coordination polyhedron around the Mn^{2+} center is best described as a distorted pentagonal bipyramid with an MnN_3O_5 chromophore.

Keywords: Schiff base; Carbonohydrazone; Manganese; X-ray diffraction; Complex; mononuclear

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I. Introduction

The symmetrical Schiff base ligands obtained from carbohydrazone react with transition metal ions to generate coordination compounds with original structures.[1–6]. Schiff bases derived from carbohydrazone and their complexes with transition metal ions are reported in the literature as good therapeutic antimicrobial anticonvulsant pharmacological and catalytic agents[7–10]. Those complexes are particularly interesting in various field such as magnetism [11–14] luminescent [15–17] and analytical chemistry [18 19]. Ligands with an amide bond can give two keto-enol tautomeric forms and can react in neutral form or in deprotonated form with a metal ion. They can coordinate with metal in several different ways due to the many coordination sites. However the behavior of these ligands depends on the metal ion on physico-chemical parameters such as the pH of the medium and the temperature and on the conformation of the hydrazone group[11 12].

In this paper we report the synthesis and structural characterization of the Mn(II) transition metal complex with the carbonohydrazone ligand (H_2L : NN'-15-bis(pyridylmethylidene) carbonohydrazone). The ligand and the complex were characterized by FTIR spectroscopy nuclear magnetic resonance (1H and ^{13}C NMR) UV-visible spectrophotometry conductimetric and magnetic measurements at room temperature. The crystalline structure of the new manganese (II) complex formulated as $[Mn(H_2L)_2(H_2O)_2] \cdot (ClO_4)_2 \cdot 3(H_2O)$ was elucidated by X-ray diffraction.

II. Experimental

2.1. Materiel and procedures

2-pyridincarbalddehyde carbohydrazone and metals transition salts were purchased from Aldrich and used without further purification. Melting points were recorded on a Büchi apparatus and uncorrected. The FTIR spectra were recorded on a Perkin Elmer Spectrum Two spectrophotometer ($4000-400 \text{ cm}^{-1}$). The 1H and ^{13}C NMR spectra of the Schiff base were recorded in DMSO- d_6 on a Bruker 250 MHz spectrometer at room temperature using TMS as an internal reference. The UV-Vis spectra were recorded in acetonitrile solution concentration of 10^{-3} M at 25°C on a Perkin Elmer Lambda 365 UV-Vis spectrophotometer. The molar conductance of 10^{-3} M solution of the metal complex in acetonitrile was measured at 25°C using a WTW LF-

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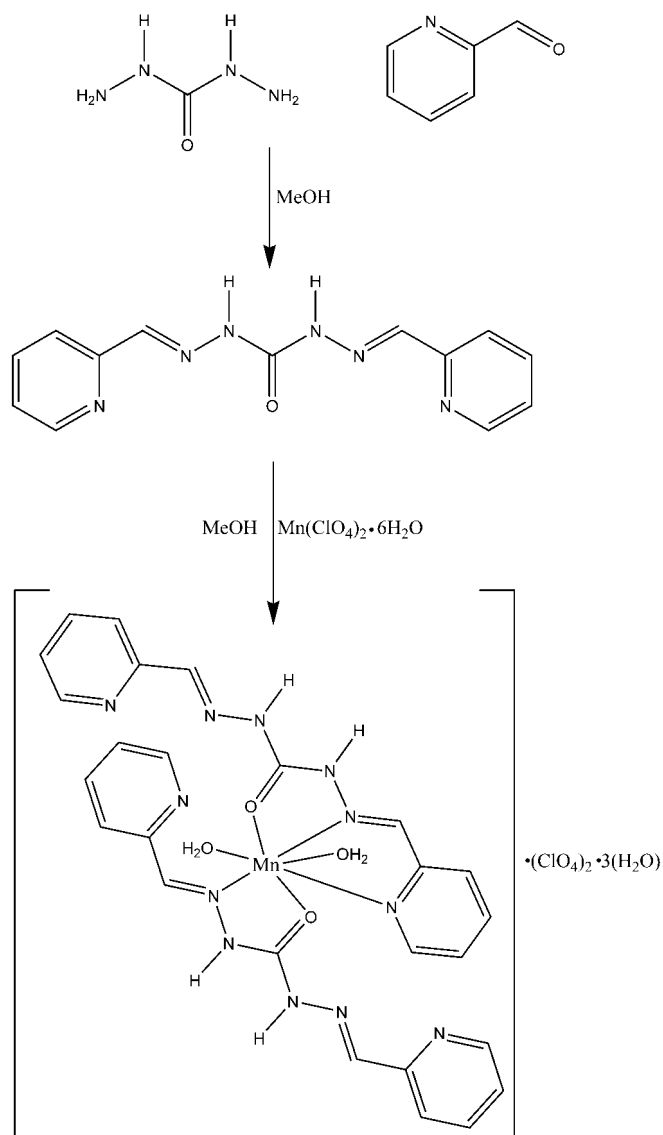
330 conductivity meter with a WTW conductivity cell. Room-temperature magnetic susceptibility of the powdered sample was measured using a Johnson Matthey scientific magnetic susceptibility balance (calibrant Hg[Co(SCN)₄]).

2.2. Synthesis of ligands N N'-15-bis (pyridylmethylidene) carbonohydrazone (H₂L)

To a solution of carbohydrazide (2g 22.2 mmol) in 20 mL of methanol was added dropwise a solution of 2-pyridincarbalddehyde (4.757 g 44.4 mmol) in 10 mL of methanol. The mixture was stirred under reflux for 2 hours. The orange solution obtained yield precipitate after two days in the refrigerator. The precipitate was isolated by filtration and successively washed with 2 × 10 mL of hot methanol and dried under P₄O₁₀. Yield: 82%. M.P : 216 ° C. Anal. calcd. for C₁₃H₁₂N₆O₂: %C 60.80; %H 5.44; %N 28.36. Found %C 60.83; %H 5.48; %N 28.32. IR (νcm⁻¹) : 3204(ν_{N-H}) 3055(ν_{C_{Ar}-H}) 1684(ν_{C=O}) 1610(ν_{C=N}) 1582-1467(ν_{C=C})_{Py} + (ν_{C=N})_{Py} 1131(ν_{N-N}). ¹H NMR (dmsO-d₆ δ (ppm)) :7.6 - 8.72 (m 8H H_{Py}) 10.82 (s 2H NH) 8.03 (s 1H HC = N). ¹³C NMR : 157.9 (C=O) 154.70 (C_{py}) 148.07 (C_{py}) 146.67 (C = N) 137.60 (C_{py}) 123.00 (C_{py}) 119.09 (C_{py}).

2.3. Synthesis of the complex [Mn(H₂L)₂(H₂O)₂].(ClO₄)₂.3(H₂O)

In a 100 mL round bottomed flask a solution of H₂L (0.2568 g 1 mmol) in 10 mL of methanol was added a solution of Mn(ClO₄)₂.6(H₂O) (0.3619 g 1 mmol) in 5 mL of methanol. The mixture is stirred during one hour at room temperature. The resulting yellow solution was filtered and the filtrate was left at room temperature. On standing for one-week crystals suitable for X-ray analysis were isolated. Yield : 68.8 % .Anal. calcd. for MnC₂₆H₃₄N₁₂Cl₂O₁₅: . Found % C 33.47; % H 3.89; % N 19.09; % Cl 8.05. Found % C 33.45; % H 3.87; % N 19.11; % Cl 8.01. MP> 280. IR(ν cm⁻¹): 3566 cm⁻¹ ν_{H₂O}; 3198 cm⁻¹ ν_{N-H}; 3081 cm⁻¹ ν_{C_{Ar}-H}; 1667 cm⁻¹ ν(C=O); 1590 cm⁻¹ ν(C=N)imine; 1527 cm⁻¹-1470 cm⁻¹ (ν_{C=C})_{Py} + (ν_{C=N})_{Py}; 1436 cm⁻¹; 1104 cm⁻¹ ν_{N-N}; 1071 cm⁻¹ ν₃(ClO₄); 620 cm⁻¹ ν₄(ClO₄). UV-vis (Acetonitrile λ (nm)) :225 334 405. Λ (Acetonitrile Ω⁻¹.cm².mol⁻¹): fresh solution : 153 ; after 15 days : 157. μ_{eff}: 5.25 BM.



Scheme 1. Synthetic procedure of the ligand H_2L and the complex $[Mn(H_2L)_2(H_2O)_2] \cdot (ClO_4)_2 \cdot 3H_2O$

2.4. X-ray data collection structure determination and refinement

Single crystals of $C_{26}H_{28}MnN_{12}O_4 \cdot 2(ClO_4) \cdot 3(H_2O)$ were grown by slow evaporation of MeOH solution of the complex. A suitable crystal was selected and mounted on a Kappa singleXtaLAB AFC12 (RINC): Kappa single diffractometer Radiation source: micro-focus sealed X-ray tube Rigaku (Mo)mm03 X-ray Source with graphite monochromatized $MoK\alpha$ radiation ($\lambda = 0.710173$). Data were collected at the temperature of 293 K. Details of the X-ray crystal structure solution and refinement are given in Table 1. The structure was solved with the SHELXT [20] structure solution program using direct methods and refined with the SHELXTL [21] software package. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined.

Table-1. Crystallographic data and refinement parameter for the Mn(II) complex.

Empirical formula	$C_{26}H_{28}Cl_2MnN_{12}O_{15}$
Formula weight	880.49
Temperature (K)	293
Crystal system	Triclinic
Space group	P-1
a (Å)	10.8879(5)
b (Å)	13.4705(6)
c (Å)	15.3934(6)
α (°)	100.846(4)
β (°)	101.676(4)
γ (°)	113.599(4)
Volume/Å ³	1932.76(16)

Z	2
$\rho_{\text{calc}}(\text{g}/\text{cm}^3)$	1.513
M (mm^{-1})	0.561
F(000)	906.0
Crystal size (mm^3)	$0.16 \times 0.04 \times 0.03$
MoK α (\AA)	$\lambda = 0.71073$
2 θ range for data collection ($^\circ$)	5.828 to 58.046
H k l ranges	$-13 \leq h \leq 13$ $-16 \leq k \leq 17$ $-20 \leq l \leq 19$
Reflections collected	29305
Independent reflections	8520 [$R_{\text{int}} = 0.0568$ $R_{\text{sigma}} = 0.0664$]
Data/restraints/parameters	8520/1/523
Goodness-of-fit on F^2	1.031
Final R indexes [$L > 2\sigma$ (I)]	$R_1 = 0.0922$ $wR_2 = 0.2538$
Final R indexes [all data]	$R_1 = 0.1491$ $wR_2 = 0.2965$
$\Delta\rho$ max $\Delta\rho_{\text{min}}$ min (e \AA^{-3})	1.05/-1.23

III. Results and discussions

3.1. General studies

The ^1H and ^{13}C NMR spectra of the ligand are recorded in d_6 -dmso. The singlets signals at 10.82 ppm and 8.03 ppm are respectively attributed to the N—H and H—C=N protons. The pyridine hydrogen atoms are revealed in the 7.6 - 8.72 region. The ^{13}C NMR reveals two characteristic signals at 157.9 ppm and 146.67 ppm which are attributed respectively to the C=O and C=N carbon atoms. The signals of the pyridine carbon atom are pointed in the range 119.09-146.67 ppm. The IR spectrum of the ligand shows characteristic bands at 3204 cm^{-1} , 1684 cm^{-1} , 1610 cm^{-1} and 1582 cm^{-1} which are respectively assigned to $\nu_{\text{N-H}}$, $\nu_{\text{C=O}}$, $\nu_{\text{C=N}}$ and $\nu_{\text{C=Npyridine}}$ [14]. Upon complexation with Mn^{2+} cation a shift of the bands $\nu_{\text{C=O}}$ and $\nu_{\text{C=Npyridine}}$ to low frequencies are observed. These facts are indicative of the involvement of the oxygen atom of the C=O function, the nitrogen atom of the azomethine function and the nitrogen atom of pyridine ring in the coordination sphere of the Mn^{2+} ion [22, 23]. The bands at 1078 cm^{-1} and 620 cm^{-1} respectively attributable to the vibration $\nu_3(\text{ClO}_4)$ and $\nu_4(\text{ClO}_4)$ are characteristic of an uncoordinated perchlorate group [24]. The molar conductivity is measured for a freshly prepared solution of complex in acetonitrile and after two weeks. The values recorded are respectively 153 and $157\ \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for the complex thus indicating electrolyte of type 2:1 [25] and good stability of this complex in acetonitrile. The electronic spectrum of the complex shows three broad bands at 225 nm, 334 nm and 405 nm. The band at 225 nm and 334 nm are due to the intraligand transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively [26, 27] and the band centered at 426 nm is attributed to LMCT [27–29]. The value of the room-temperature magnetic susceptibility of $5.25\ \mu\text{B}$ is close to the value found ($5.33\ \mu\text{B}$) for a similar complex $[\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})\text{Cl}_2]$ (H_2L is *N,N'*-15-bis(2-acetylpyridinyl)-carbonohydrazone) [30].

3.2. Description of the crystalline structure

The complex $[\text{Mn}(\text{H}_2\text{L})_2(\text{H}_2\text{O})_2]\cdot(\text{ClO}_4)_2\cdot 3\text{H}_2\text{O}$ crystallizes in the triclinic system with the space group P-1. Selected bond distances and angles are listed in Table 2. The crystal structure of the complex is depicted in Figure 1. The asymmetric unit of the compound contains a discrete $[\text{Mn}(\text{H}_2\text{L})_2(\text{H}_2\text{O})_2]^{2+}$ cation, two free perchlorate anions and three water molecules. In the discrete cation, one Mn(II) ion, two neutral organic ligand molecules and two coordinated water molecules are present. One ligand molecule acts in tridentate fashion through one pyridine nitrogen atom, one azomethine nitrogen atom and one carbonyl oxygen atom. The second ligand molecule acts in bidentate fashion through one azomethine nitrogen atom and one carbonyl oxygen atom. The tridentate ligand molecule forms upon coordination two five-membered rings of type MnNCCN and MnNNCO with bite angles of $67.80(9)^\circ$ [O1—Mn1—N8] and $68.33(9)^\circ$ [N7—Mn1—N8]. The bidentate ligand molecule forms upon coordination one five-membered ring of type MnNNCO with bite angle of $69.36(9)^\circ$ [O2—Mn1—N5]. The atoms which form the basal plane are practically in the same plane as the metal atom Mn1 ($\text{rms} = 0.0783$). The maximum deviation is observed for O2 atom, which is out of the plane by $0.1164(2)\ \text{\AA}$. The coordination polyhedron of the Mn(II) center is best described as a distorted pentagonal bipyramid with an MnN_3O_5 chromophore. The basal plane is defined by the N atom of the pyridine ring, two N atoms of the imino function and two O atoms of the carbonyl function. The apical positions are occupied by two oxygen atoms of the water molecules. The bond angles of the equatorial positions around Mn(II) are O2—Mn1—N8 = $67.64(14)^\circ$, N8—Mn1—N7 = $67.80(15)^\circ$, N7—Mn1—O1 = $80.80(14)^\circ$, O1—Mn1—N5 = $68.88(14)^\circ$, N5—Mn1—O2 = $75.22(14)^\circ$. The angle formed by the atoms in axial positions around Mn(II) is O3—Mn1—O4 = $175.95(4)^\circ$. These values are severely deviated from the ideal values of 72° and 180° for a regular pentagonal bipyramid. The sum of the equatorial angles around Mn(II) is 360.34° . In the equatorial plane, the Mn—N bond lengths [Mn1—N5 = $2.421(3)\ \text{\AA}$, Mn1—N7 = $2.413(3)\ \text{\AA}$ and Mn1—N8 = $2.301(3)\ \text{\AA}$] are longer than the Mn—O bond length [Mn1—O1 = $2.316(2)\ \text{\AA}$, Mn1—O2 = $2.193(2)\ \text{\AA}$]. The axial position bond lengths are Mn1—O3 = $2.173(3)\ \text{\AA}$, Mn1—O4 = $2.168(2)\ \text{\AA}$. These values are comparable to those reported for similar

manganese complexes [30 31].In the crystal the complex molecules are linked by hydrogen bonds giving rise to a three-dimensional network (Figure 2 Table. 3).

Numerous intramolecular hydrogen bonds of type N(hydrazinyl)—H···O(perchlorate) (N9—H9···O15) O(coordinated water)—H···Cl(perchlorate) (O3—H3A···Cl2) O(coordinated water)—H···O(perchlorate) (*ie.* O3—H3B···O13) and N(hydrazinyl)—H···N(pyridine) (N4—H4···N6) consolidate the structure. The crystal packing of the compound is stabilized by intermolecular O(coordinated water)—H···N(pyridine) (O4—H4A···N1ⁱ ; *i*= -x+1 -y+1 -z) N(hydrazinyl)—H···O(perchlorate) (N10— H10···O9ⁱⁱ ; *ii*= -x+1 -y+1 -z+1) and C—H···O(perchlorate)(Figure 3; Table 3).

Table-2. Selected bond distances [Å] and angles [°] for the Mn(II) complex.

Mn1—O4	2.168 (2)	Mn1—O1	2.316 (2)
Mn1—O3	2.173 (3)	Mn1—N7	2.413 (3)
Mn1—O2	2.193 (2)	Mn1—N5	2.421 (3)
Mn1—N8	2.301 (3)		
O4—Mn1—O3	173.59 (10)	N8—Mn1—N7	68.33 (9)
O3—Mn1—O1	84.57 (11)	O3—Mn1—N5	92.39 (10)
N8—Mn1—O1	67.80 (9)	O2—Mn1—N5	69.36 (9)
O2—Mn1—N7	78.24 (9)	O1—Mn1—N5	76.72 (9)

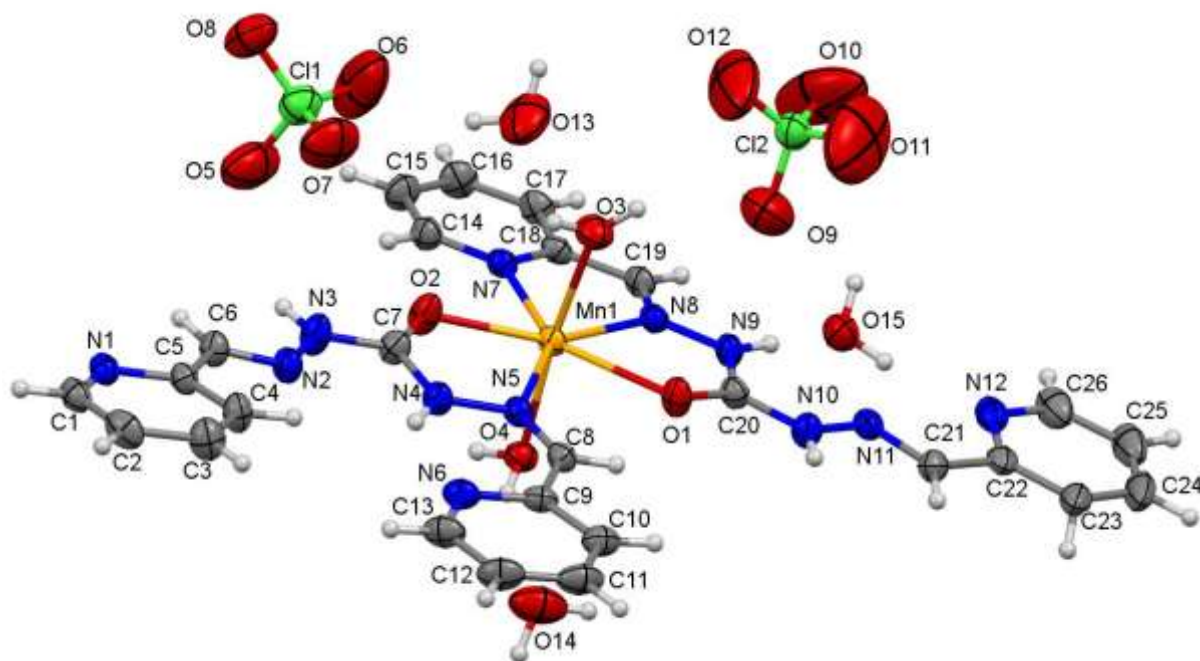


Figure 1 . Crystal structure of the complex $[Mn(H_2L)_2(H_2O)_2] \cdot (ClO_4)_2 \cdot 3(H_2O)$.

Table 2. Hydrogen-bond geometry (Å °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3A···Cl2	0.86	2.86	3.688 (3)	162.9
O3—H3A···O9	0.86	2.12	2.858 (6)	143.0
O3—H3B···O13	0.85	2.04	2.669 (5)	130.1
O4—H4A···N1 ⁱ	0.87	1.88	2.731 (4)	165.2
O4—H4B···O14	0.86	2.07	2.821 (4)	144.9
N9—H9···O15	0.86	1.99	2.831 (4)	164.1
N10—H10···O9 ⁱⁱ	0.86	2.36	3.177 (7)	158.1
N4—H4···N6	0.86	2.00	2.659 (4)	132.5
N3—H3···O5	0.86	2.37	3.014 (6)	132.1
C14—H14···O2	0.93	2.40	2.978 (4)	120.2

C19—H19...O10 ⁱⁱⁱ	0.93	2.64	3.403 (8)	139.3
C23—H23...O15 ^{iv}	0.86	2.60	3.263 (5)	134.7
C8—H8...O1	0.93	2.41	3.033 (4)	124.0
O13—H13A...O12 ^v	0.85	2.53	3.334 (10)	159.7
O13—H13B...C11	0.85	2.89	3.736 (6)	172.1
O13—H13B...O6	0.85	2.41	3.160 (10)	147.8
O13—H13B...O7	0.85	2.44	3.230 (9)	155.2

Symmetry codes: (i) $-x+1 -y+1 -z$; (ii) $-x+1 -y+1 -z+1$; (iii) $-x+1 -y+2 -z+1$; (iv) $-x+2 -y+1 -z+1$; (v) $-x -y+2 -z+1$.

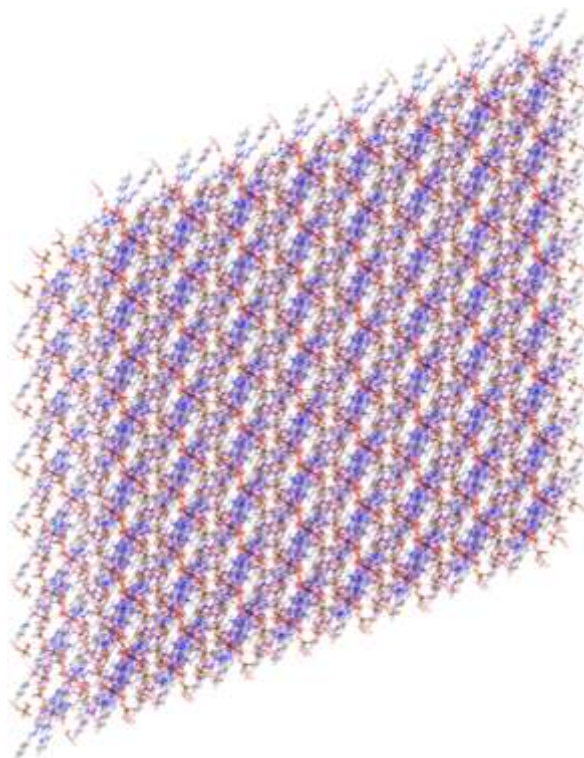


Figure 2 . Packing diagram [Mn(H₂L)₂(H₂O)₂](ClO₄)₂·3(H₂O)

IV. Conclusion

The complex [Mn(H₂L)₂(H₂O)₂](ClO₄)₂·3H₂O synthesized by the reaction of the Schiff base *NN*-15-bis(pyridylmethylidene) carbonohydrazone and hexahydrated manganese diperchlorate have been characterized by IR and UV spectroscopies conductivity and room temperature magnetic moment measurements and X-ray diffraction technic. On standing for two weeks the conductance varies slightly indicating a stable complex in acetonitrile solution. The value of the room temperature magnetic moment is in accordance with a mononuclear *d*⁵ manganese complex. In the mononuclear complex [Mn(H₂L)₂(H₂O)₂](ClO₄)₂·3H₂O the Mn²⁺ center is seven coordinated. One ligand molecule acts through one pyridine nitrogen atom one azomethine nitrogen atom and one carbonyl oxygen atom while the second ligand acts through one azomethine nitrogen atom and one carbonyl oxygen atom. The coordination sphere is completed by two coordinated water molecules. The coordination polyhedron around the Mn (II) center is best described as a distorted pentagonal bipyramid. The molecules are linked together in each case by numerous hydrogen-bonding interactions resulting in a three-dimensional network.

Supplementary Materials

CCDC-[2266947](https://www.ccdc.cam.ac.uk/structures/or) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/or> by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre 12 Union Road Cambridge CB2 1EZ UK; fax: +44(0)1223-336033.

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