International Journal of Current Research in Chemistry and Pharmaceutical Sciences
www.ijcrcps.com Volume 1 Issue: 5 2014 Pages:84-88
(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

RESEARCH ARTICLE

HYDROTHERMAL SYNTHESIS OF Mn-IDA METAL-ORGANIC FRAMEWORK

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Abstract

A new metal-organic framework Mn–IDA (manganese imino diacetate) was synthesised and it is found out to have an orderly arranged fashion known by x-ray crystallographic studies. The ordered arrangement and the cell volume suggested that there is enough volume for guest sorption. The hydrogen bonds through coordinated water extended in all directions to give a three dimensional structure.

Keywords: Metal-organic framework; Mn-IDA; ordered arrangement.

Introduction

Metal-organic frameworks are of great interest for their sorption characteristics. Metal-organic frameworks will have identical connectivity, ordered rings and contains cavities in which guests can be accommodated. For example Rosseinsky and co-workers have found that the guests can be incorporated into a nickel pyridine framework. Fujita and co-workers have reported dramatic changes in structure induced by guest sorption involving the sliding of layers and also 20% volume change in another case.

Wright and co-workers reported that H-bonding molecules can be included into Zn(II)-benzenedicarboxylate networks leading to reconstruction of the networks into new and distinct connectivities.

Stuart L. James and his co–workers have synthesised Manganese isonicotinate hydrothermally and the crystal structure reveals that it is monoclinic with a space group P21/c. The structure consists of Mn(II) centres doubly bridged by carboxylate groups into infinite chains, with the pyridine functions of the INA ligands pointing out from the chains. The rings in $Mn(INA)_2$ are ordered. At the open rings in $Mn(INA)_2$, there is sufficient space to accommodate guest molecules. Similarly Stuart L. James and his co-workers have also synthesised cobalt-isonicotinate metal-organic framework hydrothermally and the crystal structure reveals that it is monoclinic with a space group P21/n. The small size of the windows in the channels suggests that the framework structure must be able to distort significantly to allow the guests to pass out. The fact that the pyridyl rings have different conformations in ethanol solvated and desolvated structure shows that some rotation (M-IDA) (M=divalentmetal ion, IDA=iminodiacetate). The compound Mn–IDA has an identical connectivity and contains cavities in which guests can be accommodated.

Experimental

Synthesis of Mn-IDA was done by taking 0.5 mmol of Manganese acetate and 0.5 mmol of imino

diacetic acid. Manganese acetate was dissolved in water separately. Imino diacetic acid was dissolved in a mixture containing 10ml of ethyl alcohol and water. Both the solution are mixed and taken in a Teflon coated autoclave. It is heated to 150^0 C for 12 hours. Colourless crystals were obtained which was washed with dry diethyl ether and dried. Elemental analysis for the compound has been done and reported below.

Crystal data

Atoms are in the ratio $C_8H_{16}N_2O_{10}Mn$ which corresponds to the formula $Mn(IDA)_2{\cdot}2H_2O$ M= 355g/mol. The crystal has tetragonal symmetry with the space group P-421c with sides a = 8.0990, b = 8.0990, c = 9.6040 and with angles $\alpha = 90^0$, $\beta = 90^0$ and $\gamma = 90^0$. It has call volume of $629.7A^0$. The number of atoms per unit cell is (Z) = 8 with total number of 3168 reflections collected.

Results and Discussion

The title compound $Mn(IDA)_2{\cdot}2H_2O$ crystallizes in tetragonal space group P-421c. In the molecular structure the Mn atom occupies the special position along 4 – fold rotation axis. The asymmetric unit of the title compound consists of half imino diacetate moiety co-ordinated to the Mn atom. The N – atom of the IDA moiety lies along the two fold rotation axis. The molecular structure of $Mn(IDA)_2$ complex is shown in figure 1 & 2. The molecular structure consists of Mn(II) centers bridged by carboxylate group through the co ordinate oxygen 02 at -x, -y, z, 02 at y -x, -z+1 and –y,x,-z+1 to generate a two dimensional coordinated complex sheet along (00 1) plane. The N atom in the two fold axis also takes part in the extended two dimensional sheet through the equivalence –x+1, -y, z. The manganese ions at the special position show distorted octahedral geometry with the Mn1…02 distance of $2.1848A^0$ and the Mn1…..01 distance of $2.1448A^0$. (coordinated water molecule). The 01 – Mn – 02 angles makes a slight deviation from 90^0 with a value of $83.49A^0$. The molecular co-ordination of imino diacetate anion with the Mn (II) ion forms an interesting molecular two dimensional framework.

The N–H **…**0 hydrogen bond N1-HIA…03#6 (#6: -y+1, x,-z+1) also the part of the network with D…. A distance of $2.9224A^0$. Parallely stacked molecular sheet along c – axis are further interlinked through O – H**….**O hydrogen bonds through the coordinated water molecules. The hydrogen bond with D….A distance $2.7001A^0$ interconnect to generate a three dimensional molecular network which constitute the packing in the crystalline solid.

The formulation also fit well with the thermogravimetric analysis of the crystal which showed a weight loss of 10.25% on heating from 0^0C to 210^0C which is similar to the 10.14% calculated for the water molecule present in the crystal. The TGA curve is shown in figure 3. The IR spectrum showed a peak around $3752cm^{-1}$ which corresponds to O–H stretching of alcohols. Another absorption in the region $3055cm^{-1}$ corresponds to CH_2 group. The peak around $1612cm^{-1}$ corresponds to asymmetric stretching of the COO^- group. Another peak in the region $1370cm^{-1}$ corresponds to symmetric stretching of the COO^- group. The difference (242) between both vibrations suggests fundamentally covalent character of the ligand-metal bonding. Absorption in the region $1057cm^{-1}$ corresponds to C–N stretching. The IR spectrum is shown in figure 4 and the IR absorption frequencies are given in table 2.

The powder x-ray diffraction pattern of the bulk was similar to the one simulated from the single crystal diffraction data using mercury 2.3 software which reveals that they have similar structures. The XRPD pattern is shown in figure 5a and 5b.

Table 1. Elemental Analysis

Name of the crystal	C	H	N
Manganese imino diacetate (experimental)	27.39%	3.76%	7.78%
Calculated	27.09%	3.94%	7.88%

Table 2. IR Absorption Frequencies

	OH	CH_2	O C O^-	C-O	C-N
Mn-1DA crystal	3752 cm^{-1}	3085 cm^{-1} 1415 cm^{-1} 925 cm^{-1}	1612 cm^{-1} asym 1370 cm^{-1} sym	1267 cm^{-1}	1057cm^{-1}

Fig. 1 Three dimensional structure of Mn-IDA involving hydrogen bond.

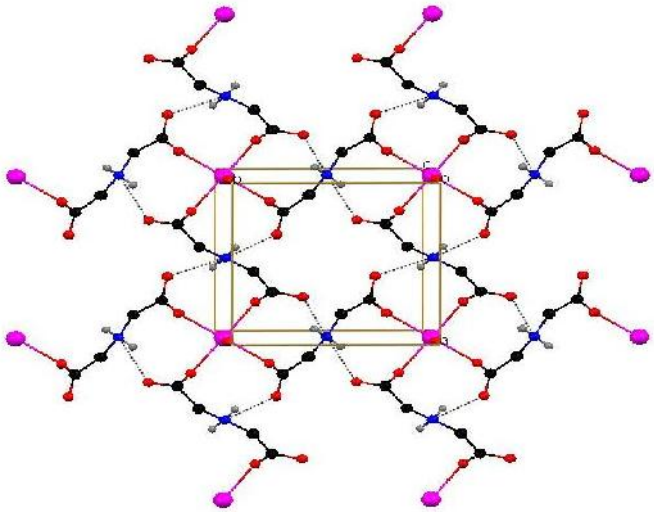


Fig. 2 Two dimensional structure of Mn-IDA.

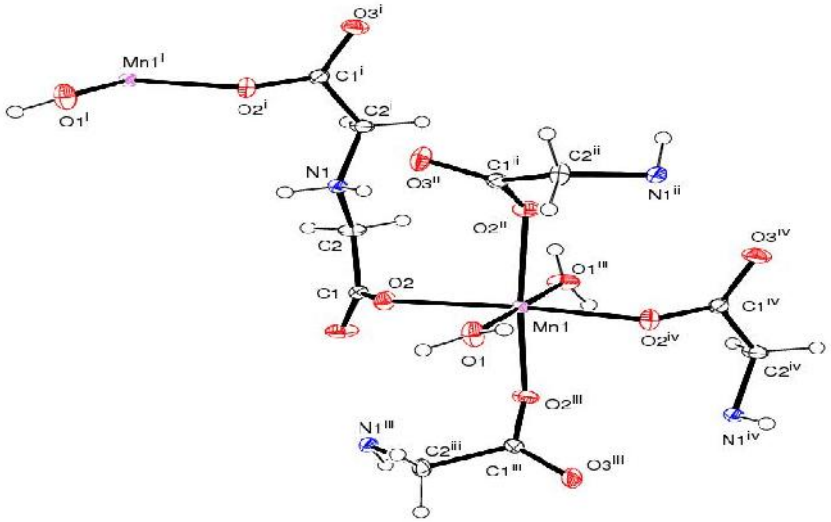


Fig. 3 TGA of Mn-IDA Crystal

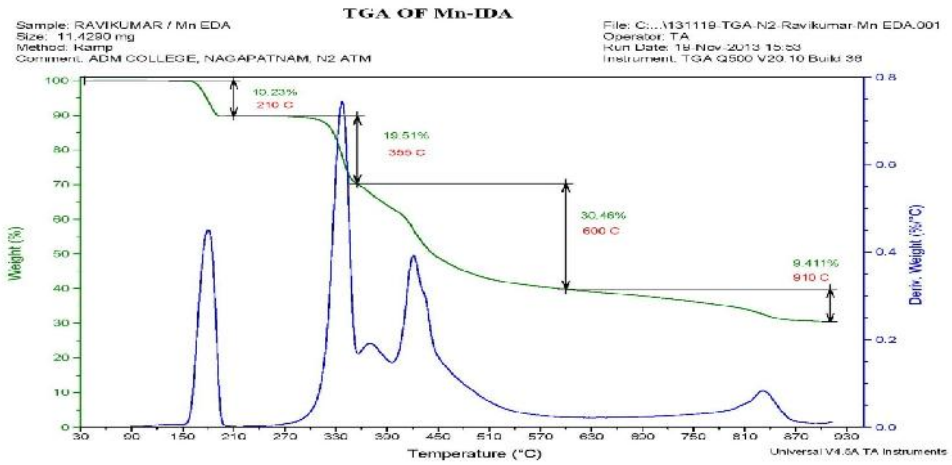
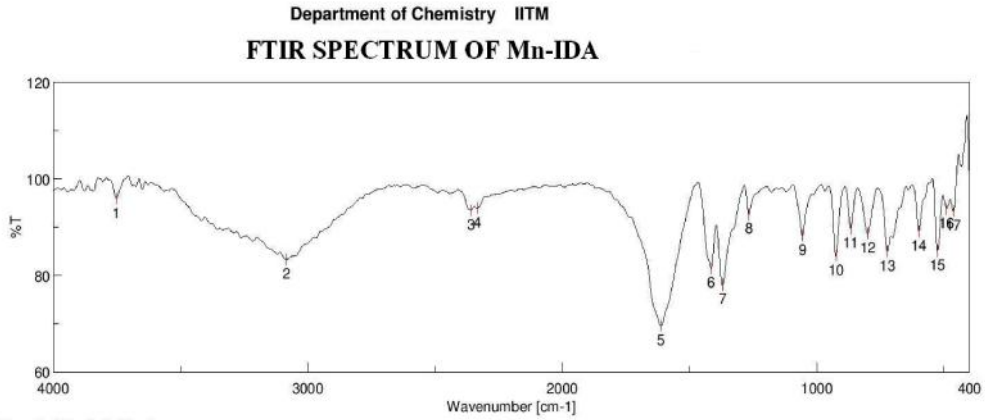


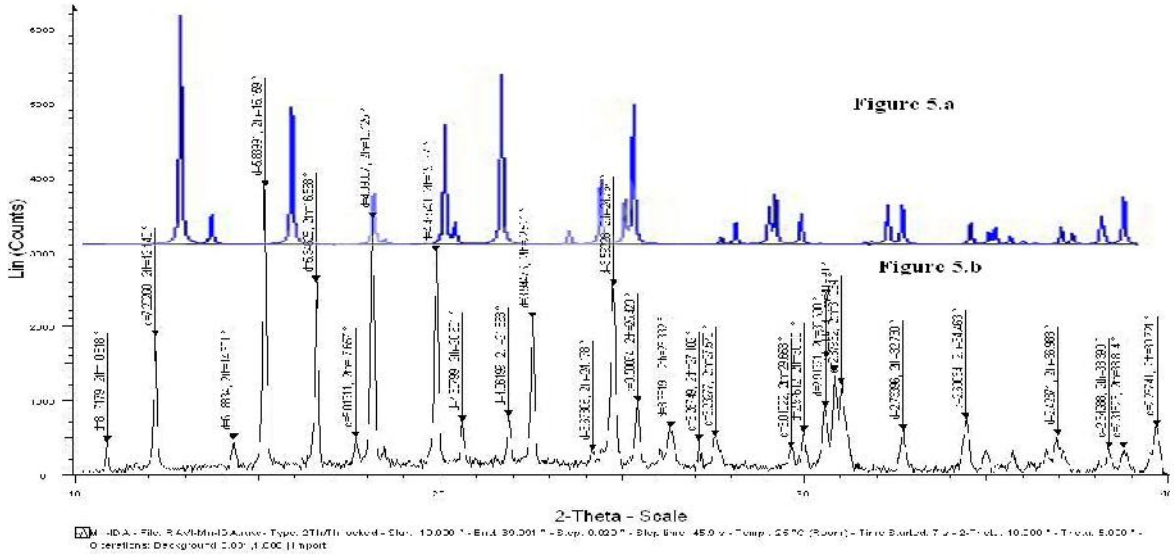
Fig. 4 FTIR spectrum of Mn-IDA Crystal



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3752	95.8449	2	3085	83.2792	3	2358	93.4513	4	2334	93.8402
5	1612	69.5107	6	1415	81.4022	7	1370	77.9469	8	1267	92.5985
9	1057	88.2303	10	925	83.9694	11	867	89.6182	12	800	88.6517
13	722	84.8713	14	599	89.0149	15	526	84.9781	16	490	93.7373
17	463	93.213									

Fig. 5a & 5b. XRPD of Mn-IDA Crystal and the simulated pattern of the crystal.



Conclusions

$Mn(IDA)_2{\cdot}2H_2O$ is a Metal-organic framework found to have solvent filled cavities. The IR spectrum reveals that there are two absorptions corresponds to the coordinated COO^- group. The TGA curve showed a weight loss of 10.25% on heating from 0^0C to 210^0C which is similar to the 10.14% calculated for the water molecule present in the crystal. The cell volume of the structure ($629.7A^0$) suggests that there is enough space for the absorption of guests.

Acknowledgements

i).The authors are grateful to the single crystal diffraction centre IIT-Madras for their technical support.
ii).The authors are grateful to the department of chemistry IIT-Madras for helping in taking out XRPD, TGA, FTIR, and CHN analysis.
iii).The authors are grateful to the Anna university crystal growth centre for taking SEM images and EDAX analysis.

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