Hydrothermal Synthesis and Single Crystal X-ray Diffraction Studies of a new Magnesium based Metal – Organic Coordination Networks

A

Thesis Submitted

in partial fulfilment of the requirements for the award of the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

BY

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JULY, 2013

Certificate

This is to certify that the project entitled **"Hydrothermal Synthesis and Single Crystal X- ray Diffraction Studies of a new Magnesium based Metal – Organic Coordination Networks"** being submitted by Naveen Kumar, Roll no. 301102005 in partial fulfillment of the requirements for the award of degree of Master of Science in School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under my supervision and guidance. The report has not been submitted for the award of any other degree or certificate in this or any other university.

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Candidate's Declaration

I hereby declare that the work which is being presented in the dissertation entitled "**Hydrothermal Synthesis and Single Crystal X- ray Diffraction Studies of a new Magnesium based Metal – Organic Coordination Networks**" in partial fulfillment of the requirements for the award of the degree of master of science in Chemistry, School of Chemistry and Biochemistry, Thapar University, Patiala is an authentic record of my own work during a period of six months from January 2013 to July 2013, under the supervision of Dr. Partha Mahata, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. The report has not been submitted for the award of any other degree or certificate in this or any other university.

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This is to certify that the above statement given by the candidate is correct and true to the best of our knowledge.

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Acknowledgement

In pursuit of this academic endeavor, I feel that I have been singularly fortunate because inspiration, guidance, direction, co-operation, love and care all come in my way in abundance and it seems almost an impossible task for me to acknowledge the same in adequate term.

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Life at Thapar University would be unforgettable for me throughout my life because I was blessed to spend it with my friends. I thank them all for their great company.

Words fail me to express my thanks to my family for their selfless sacrifice, encouragement and heart full blessings that continue to enlighten my life.

Above all I thank almighty God for blessing me with strength and wisdom to complete this project successfully.

Naveen Kumar.

Naveen Kumar

Contents

Introduction and review of literature

Introduction

The compounds having open structures are one of the most important family of solids due to their use in the areas of ion-exchange, separations, and catalysis.[1,2] At the bottom of the synthesis of such structures lies the idea of rational design that involves the assembly of small molecular units to obtain the desired solid. Though most of the early network compounds belong to the silicates, the real breakthrough in this area is due to Flanigen and co-workers during the early 1980s.[3] The synthesis of the first zeolite-analogues in the family of microporous aluminophosphate solids ($ALPO_4$-n, where n refers to a structural type) is a land mark discovery in this area.[3] This paved the way for further research resulting in many different varieties of framework compounds involving almost all the elements of the periodic table. During the 1990s the clever combination of the coordination preference of the metal ions and the functionalities of the organic molecules gave rise to another interesting series of compounds that are now being called metal-organic coordination network compounds.[4] In the light of this, it is important to note the seminal work of Robson in this area.[5] Over the past decade, several new types of compounds embracing the majority of the elements of the periodic table exhibiting a wide range of structures and properties have been synthesized. Attempts are also made to exploit the newly discovered metal-organic coordination network (MOCN) compounds for their pore-related properties, which appears to be promising and exciting. The salient features of some of the MOCN compounds are presented here.

In this overview, the history and summary of the various types of network compounds are also given for better appreciation of the evolution of such structures in the literature.

Zeolites and zeolite-like materials

The discovery of aluminosilicates, well known as zeolites, was by Cronstedt and dates back to as early as 1756.[6] However, the development of the field of microporous materials occurred after the first synthesis of the artificial zeolites in 1948, by Barrrer.[7] Since then numerous compounds with zeolitic structures have been prepared and characterized. The growth in this area can be evidenced from the large number of reviews and related articles published in the literature.[1]

Zeolites are microporous crystalline aluminosilicates, composed of TO_4 tetrahedra (T = Si, Al) with oxygen atoms connecting the neighbouring tetrahedra. The TO_4 tetrahedra are close to being regular, but the T – O – T angles about the apical oxygen atoms can accommodate values ranging from ~125° to 180°, which is one of the reasons for having so many different structures for the zeolites. For a completely silicious structure, the SiO_4 units alone are connected forming a solid with a general formula SiO_2, which is an uncharged solid. Upon incorporation of Al into the silica framework, the +3 charge on the Al makes the framework negatively charged, which requires the presence of extra framework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral. The general formula of zeolite can be written as $M^{m+}{}_{n/m}$ $[(AlO_2)_x(SiO_2)_2]^{x-}.nH_2O$, where M represents the extra-framework cations, m represents the cation valence, $[(AlO_2)_x(SiO_2)]^{x-}$ represents the anionic framework and the water is the sorbed phase. The framework has a oxygen/tetrahedra ratio of 2 and the presence of Al atoms in the framework gives rise to a net negative charge of x, which can be varied by changing the Si/Al ratio. The value of x is equal to or greater than 2 because Al^{3+} does not occupy the adjacent tetrahedral sites and Al – O – Al type of linkages are not favoured (Loewenstein's rule).[8] The variation of Si/Al ratio is important for the acidic properties of the zeolites. The crystalline framework structures of zeolites contain voids and channels of different shapes and sizes. The pore or channel opening ranges from 3 – 8 Å depending on the structure of the zeolite. The net negative charge of the framework is neutralized by the presence of extra framework cations. The cations include the alkaline (Na^+, K^+, Rb^+, Cs^+), alkaline earth (Mg^{2+}, Ca^{2+}), NH_4^+, H_3O^+, organic amines TMA^+ (tetramethylammonium), rare earth and other metal ions and some nitrogen containing compounds. The organic amine cations can act as a template and it is believed that the size and the shape of the amine molecules are crucial in determining the pore structure of the zeolite. The extra framework cations are exchangeable by the treatment with suitable salt solution or molten salt.

$AlPO_4$ (AlPO) is iso-electronic with SiO_2 and can be regard as the III – V analogue with Al and P adopting the tetrahedral coordination as silicon in SiO_2. The discovery of aluminophosphate is probably the most notable discovery in the past 25 years in the area of porous solids.[3]

The structural chemistry of AlPO's is generally different from that of aluminosilicate zeolites, though there are a number of AlPOs which have zeolitic structures. First in AlPOs, the Al atoms can take four, five and/or six coordination with oxygen,[9] whereas in aluminosilicates Al atoms, generally, adopts the tetrahedral geometry. The P atom in AlPOs can share one, two, three or four oxygen atoms with the adjacent Al atoms. The Si/Al ratio in zeolites is dependent on the states and distribution of polysilicate anions in the framework. Second, the strict alternation of Al and P tetrahedra in AlPO's can form rings with even number of T atoms such as 8, 12, 14, 18 and 20, whereas in aluminosilicate zeolites, five-ring units are seen. Third, the AlPO structures are obtained by employing organic amine templates which interact with the frameworks through the hydrogen bonds. The Al – O and P – O bonds are internally weaker and hence some of the AlPO's are not thermally stable compared to the aluminosilicate zeolites.

Metal-organic network compounds

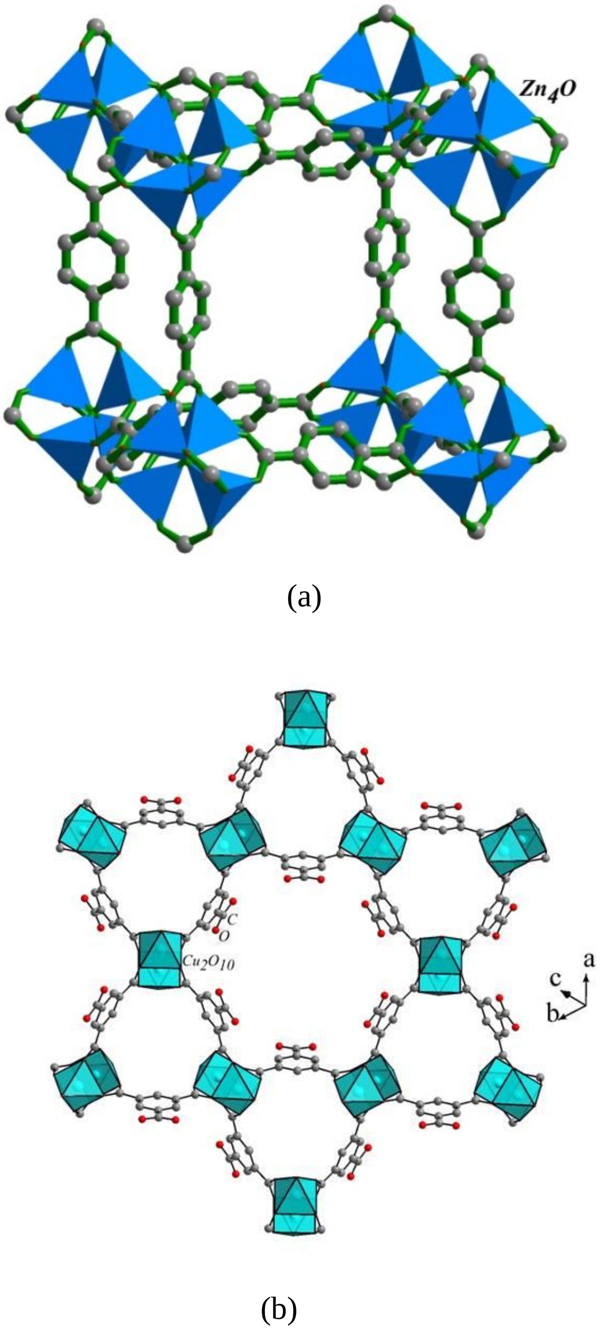
Metal-organic network compounds constitute an important class of materials that have been studied extensively over the last few years as they offer great potential for applications in the areas of catalysis, gas separation and storage.[4] Other properties that can be conceived with this class of materials include magnetic, optical and electronic properties.[4] It is necessary to understand the place of MOCN compounds relative to the conventional coordination compounds. The pioneering work of Werner on the coordination compounds and the subsequent developments in their chemistry was the foundation over which the field of coordination networks is built, which exhibit rich and varied chemistry. Thus, the coordination compounds constructed using the metal ions as connectors and ligands as linkers can be referred to as coordination networkss.[9] This term was first used in the early 1960s, and this area was first reviewed in 1964.[10]

Intense research over the years produced compounds with one, two and three dimensional structures. The coordination networks are connected through coordination bonds, which are weaker, compared to the strong Si/Al-O bonds of zeolites. Thus, coordination networks have poor thermal stability but are sufficiently robust for many applications. The use of organic carboxylate liagnds for forming extended frameworks was first demonstrated by Robl in 1987.[11] Robson, Hoffman and Yaghi, recognized that rigid, polyfunctional organic molecules could be employed to bridge the metal cations or clusters into extended arrays.[4] In this connection, the paper in the field of crystal engineering – the science of predicting basic networks with potentially useful characteristics and then using appropriate molecular building blocks to synthesize them by Robson is importnat.[5,12,13] The molecular building block (MBB) approach was developed later by Wuest[14] and Hosseini,[15] using molecular tectonics (from tekton, the Greek word for builder), in which multiple peripheral sites with strong directional interaction of a molecules is utilized.[16] This leads to the development of predictable architectures by designing pre-arranged and active molecular tectons. For designing porous MOCNs, networks can be envisioned based on rigid organic molecules and metal atoms or clusters.[18] Several groups have focused on the synthesis and characterization of new MOCN compounds using various organic ligands especially carboxylates and nitrogen containing heterocyclic compounds.[1a,19] The reviews by Mahata and Natarajan, Robson and Batten,[20] Yaghi and O'Keeffe,[21,22] Schröder,[23] and others reflect the importance of the structural variety and properties offered by MOCN compounds.

Structure of MOCNs

The structure is an important aspect in inorganic materials chemistry. Structure of the metal – organic coordination networks determines the nature of the pores, which can be exploited for many important applications. It has been suggested that the formation of a particular structure can be controlled by careful design of the participating ligands, but in practice it is not very easy. Yaghi and coworkers have employed the close similarity between the – Si – O – Si angles to that of the – N – C – N – angle in imidazole to prepare a variety of zeolite – like imidazolate frameworks.[24] This can be considered as a reasonable success of the design based synthetic approach. The other way to understand the structure is to view the complex MOCN structures as that derived from classical inorganic structures.[25] The variations in the coordination modes of the participating organic functional groups along with the coordination geometry preferences of the central metal ions makes it difficult to predict, apriori, the final structure of the MOCNs. In spite of these difficulties, there has been considerable progress in identifying important inorganic structures within MOCNs. Here, we present few examples of some of the important MOCN structures.

The most studied/well known MOCN structures are MOF-5,[26] HKUST-1,[27] MIL-53,[28] MIL-101.[29] Many of these are high symmetry structures and have periodic well connected pore structures. The MOF-5, $[Zn_4O(1,4\text{-bdc})_3(DMF)_8(C_6H_5Cl)]$, can be considered as derived from the α-Po structure (Figure 1a). It has been shown that this structure is amenable to manipulation and can be considered as a generic structure for a family of similar compouns.[30] The HKUST-1, $[Cu_3(btc)_2]$, on the other hand has a unique structure (Figure 1b). It is now possible to synthesize this compound by careful layer – by – layer assembly which can be exploited for many practical purposes.[31] The MIL (MIL=Materials of Institute Lavoisier), is another large family of compounds exhibiting interesting structures. Unlike MOF-5 structure, the MIL-53 structure is stabilized using a large number of elements of the periodic table.[32] Thus, these representative structures clearly demonstrate the vast potential for structural manipulations: the MOF-5 structures exhibit manipulation of the organic while the MIL structures exhibit elemental (inorganic) manipulations.



(a)

(b)

Figure 1: (a) The structure of MOF-5, showing the connectivity between the Zn_4O clusters and 1,4-bdc units, (b) The structure of HKUST-1, showing the connectivity of the trimesate with the copper paddlewheel.

The addition to these structures, the homochiral structures prepared by Kim and co workers,[33] $[Zn_3(\mu_3\text{-}O)(\mathbf{L_4}\text{-}H)_6]\cdot 2H_3O\cdot 12H_2O$ suggest that non – centrosymmetric structure with periodic porosity can be prepared easily. These may find useful applications in chiral reactions and separations and constitute an important development in MOCNs. Kitagawa and co-workers recently utilized the concept of mutual recognition of common crystallographic planes with comparable lattice parameters to synthesize hetero structures with MOCNs. The compound [$Zn_2(ndc)_2(dabco)$] is used as the core crystal over which the compound [$Cu_2(ndc)_2(dabco)$], is grown. This is a completely new concept and represents the first example of a hetero – structure in MOCN. Both the phases have the same space group and possess near identical lattice parameters, which resulted in the possibility of the epitaxial growth of one phase over the other.[34]

It is becoming clear that the MOFs, not only have interesting crystal structures that can be viewed as a derivative structure of the classical inorganic ones, but also are amenable for manipulations. The variety and diversity of MOF structures appears to be unique.

Synthesis of MOCNs

Hydrothermal synthesis

"Hydrothermal synthesis" usually refers to any heterogeneous reaction in aqueous media above 100ºC and 1bar. The previously common distinction between hydrothermal conditions and pneumatolytic conditions below and above the critical point is no longer made, since no discontinuities are observed upon exceeding the critical temperature and pressure. Under hydrothermal conditions, reactants otherwise difficult to dissolve go into solution as complexes, in whose formation water itself or very soluble "*mineralizers*" can participate. For sparingly soluble compounds with high melting point, a highly soluble transport substance is added to increase the "solubility", which is termed as "*mineralizer*". Thus, one can obtain the conditions of chemical transport reaction,[35] of which hydrothermal synthesis can be considered a special case. The role of hydrothermal synthesis in preparative solid state chemistry and crystal growth has been reviewed by Rabenau and Laudise.[36]

Hydrothermal synthesis, in contrast to conventional synthetic methods offers a number of advantages. For example, (i) Synthesis of compounds with elements in oxidation states that are difficult to attain; (ii) The hydrothermal method is also useful for the synthesis of so-called "low-temperature phases"; (iii) The most important is the synthesis of so-called metastable compounds. The various new materials synthesized under hydrothermal conditions have been reviewed recently by Feng and Xu.[37]

Water as a reaction medium

The physical and chemical properties of water and aqueous solutions in the pressure and temperature ranges required for hydrothermal synthesis are important to understand what happens in a hydrothermal autoclave. The PVT data for water up to 1000°C and 10bar are known accurately. Figure 2 shows a temperature-density diagram of water with pressure as a parameter. The viscosity decreases with temperature, at 500°C and 100 bar amounting to 10% of its value under normal conditions. Hence the mobility of molecules and ions in the supercritical range are much higher than under normal conditions. When using water as a solvent, the dielectric constant is important. The dielectric constant of water decreases with rising temperature and increases with rising pressure, the temperature effect predominating. Electrolytes which are completely dissociated under normal conditions will therefore tend to associate with rising temperature, and for a large number of substances this transition lies between 200 and 500°C.[38]

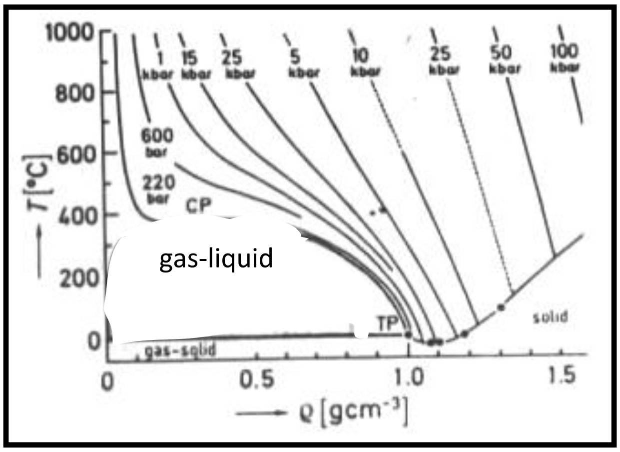
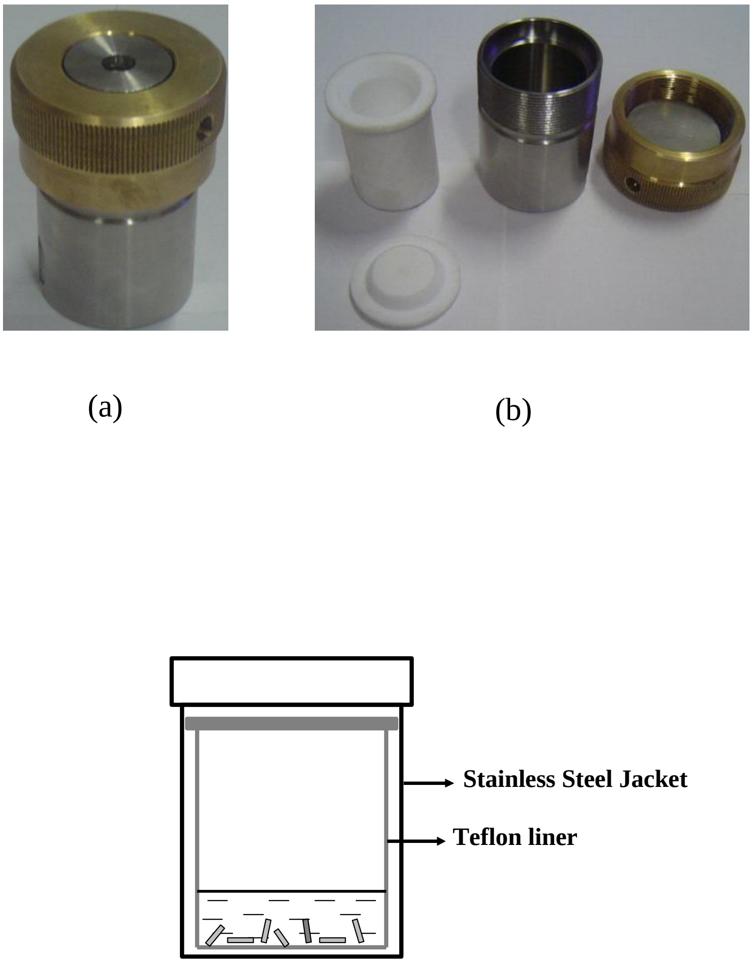


Figure 2: Temperature density diagram of water (CP and TP signify critical point and triple point respectively).

Autoclaves

To withstand the pressures involved in hydrothermal synthesis the use of autoclaves is usually required. They serve to protect the reaction vessel often the autoclave itself plays the role of the reaction vessel. Initially the autoclaves were made of steel with noble metal lining. In recent years further variation using *Teflon* as a material for reaction vessel was described by Herdtweck[39] for studies with hydrofluoric acid. Since under pressure teflon tends to become porous, only isostatically treated potentially pore-free material (PTFE) can be used. Autoclaves with teflon inserts are now widely used as digestion bombs (Figure 3) and are commercially available.[40] Quartz glass ampoules for hydrothermal investigations are also described by Speed and Filice.[41]



(a) (b)

(c)

Figure 3: (a) The external view of the autoclave used for the synthesis described in this thesis with teflon inserts used as digestion bombs; (b) Different parts of autoclave; (c) Schematic of a cross-sectional view of the reaction vessel.

Single crystal structure determination

Single crystal structures provide unambiguous three-dimensional molecular structures of new crystalline compounds. Besides conforming the connectivity and the stereochemistry of the molecules, crystal structures obtained can give precise bond length and angle information, absolute configuration (if appropriate) and an agreement of molecules within the crystalline lattice. The single crystal structure were determined using a Siemens smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoK$_\alpha$ radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. The diffractometer operates on a PLATFORM – three-circle goniometer for precision movement of the crystal in ω and φ plus an automatic 2θ range for the detector and a two-dimensional Charge-coupled Device (CCD) detector with a 9 cm diameter input imaging area.

All the compounds were characterized using single crystal X-ray diffraction. A suitable crystal of the material was carefully selected under polarizing microscope and glued to a thin glass fibre with cyanoacrylate (super glue) adhesive. The crystal has to meet two main requirements for X-ray data collections: (i) it must possess uniform internal structure, and (ii) it must be of proper size and shape.[42] To fulfil the first requirement, a crystal must be pure at the molecular, ionic or atomic level. It must be a single crystal in the usual sense, i.e. it should not be twined or composed of microscopic sub-crystals. The existence of two different orientations of a lattice, in one crystal, is called twining. The crystal should not be grossly fractured, bent or otherwise physically distorted. The preferred crystal size is 0.1 – 0.3mm, but should not exceed 0.5 x 0.5mm. A 2.4 kW sealed tube X-ray source (Mo-K_α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The diffractometer operates on a PLATFORM – three-circle goniometer for precision movement of the crystal in ω and φ plus an automatic 2θ range for the detector and a two-dimensional Charge-coupled Device (CCD) detector with a 9 cm diameter input imaging area. Data were collected with ω scans of width 0.3°. A total of 606 frames were collected in three different settings of φ (0°, 90°, 180°) keeping the sample-to-detector distance fixed at 6.03cm and the detector position (2θ) fixed at -25°. The structure was solved by direct methods using *SHELXTL-PLUS*[43] suite of programs and difference Fourier synthesis.

An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS[44] program. In most of the cases, the hydrogen positions are initially located in the difference Fourier maps, but for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. In case of distorted molecules, restraints for the bond distances have been used to keep the molecule intact and within reasonable limits. The last cycles of refinements included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F|^2$ was carried out using the WINGX[45] package of programs.

Results and Discussion

In an attempt to synthesize metal-organic network compounds using 4,4'-oxybis(benzoate), 1,10-phenthroline and magnesium, a new compound one-dimensional structures has been discovered. This part of the thesis describes single crystal X-ray structure and powder X-ray diffractions studies of the hydrothermally synthesized compound, $[Mg(H_2O)\{C_{12}H_8O(COO)_2\}\{C_{12}H_8N_2\}]$, **I**.

Suitable single crystals of **I** was selected carefully and the structure determination carried out following the procedure described earlier [Page 8]. The relevant details of the structure determination and final refinements are listed in Table 1.

Table 1: Crystal Data and Structure Refinement Parameters of compound **I**

Empirical formula	$C_{26}H_{18}MgN_2O_6$
Formula weight	586.74
crystal system	Triclinic
space group	P-1 (No. 2)
a (Å)	7.7199(16)
b (Å)	11.532(2)
c (Å)	13.396(3)
α (deg)	82.734(4)
β (deg)	83.402(4)
γ (deg)	72.680(4)
Volume (Å^3)	1125.6(4)
Z	2
T (K)	293(2)
ρ_{calc} (g cm^{-3})	1.413
μ (mm^{-1})	0.126
θ range (deg)	1.86 to 28.03
λ (Mo K_α)	0.71073 Å

R indices [I >2σ(I)]	$R_1 = 0.0554$, $wR_2 = 0.1141$
R indices (all data)	$R_1 = 0.0923$, $wR_2 = 0.1292$

$R_1=\sum\|\|F_0\|-\|F_c\|\|/\sum\|F_0\|$; $wR_2=\{\sum[w(F_0^2-F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.$w=1/[\rho^2(F_0)^2+(aP)^2+bP]$ $P=[\max(F_0,0)+2(F_c)^2]/3$, where a = 0.0363 and b = 0.4527 for **I**.

Single crystal X-ray diffraction results shows that the structure of the complex possesses a one-dimensional connectivity and crystallizes in the space group of *P*-1. The asymmetric unit of **I** consists of one crystallographically independent octahedrally coordinated Mg^{2+} ion, one 4,4'-oxysbis(benzoate) anion, one 1,10-phenthroline and one coordinated water molecule (Figure 4).

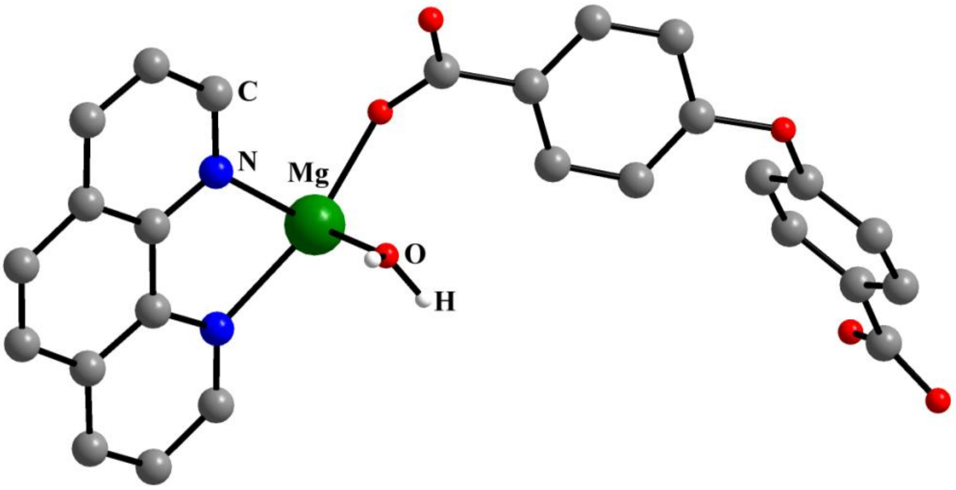


Figure 4: The asymmetric unit of compound **I**.

The Mg(1) is coordinated by three carboxylate oxygen atoms [O(2), O(2)#, O(3)], one coordinated water [O(1)] and two nitrogen atoms of the 1,10-phenthroline (Figure 5). The average Mg-O and Mg-N bond distances are 2.057 Å and 2.223 Å, respectively and the O/N-Mn-O/N bond angles are in the range of 78.32(7)-171.11(7)°. Out of the two carboxylate groups of the OBA anion, one is coordinated with two Mg^{2+} ions through O(2) and the other carboxylate group is coordinated with one Mg^{2+} ion (Figure 6). The selected bond distances and angles for **I** are listed in Table 2 and 3.

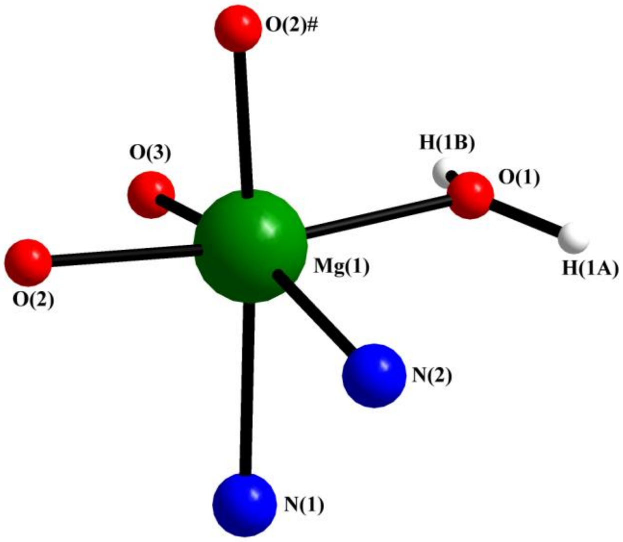


Figure 5: The coordination environment around Mg^{2+} ion in **I**.

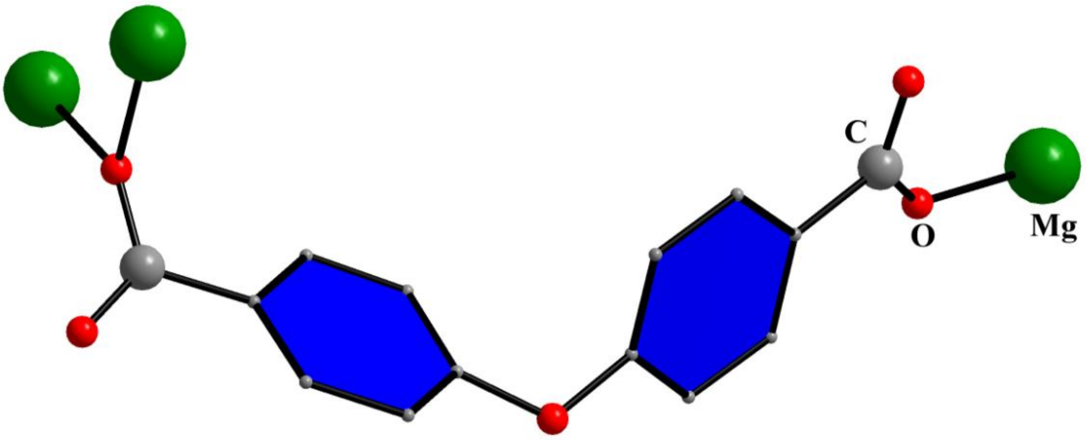


Figure 6: The binding mode of the OBA anion with the Mg^{2+} ions in **I**.

Table 2: Selected Bond Distances (Å) observed in compound **I**.

Bond	Distance	Bond	Distance
Mg(1)-O(3)	2.0251(16)	Mg(1)-O(2)#1	2.0984(17)
Mg(1)-O(1)	2.0486(19)	Mg(1)-N(2)	2.2055(19)
Mg(1)-O(2)	2.0569(16)	Mg(1)-N(1)	2.240(2)

Symmetry operation used to generate equivalent atoms for I: #1 –x, -y+1, -z+2

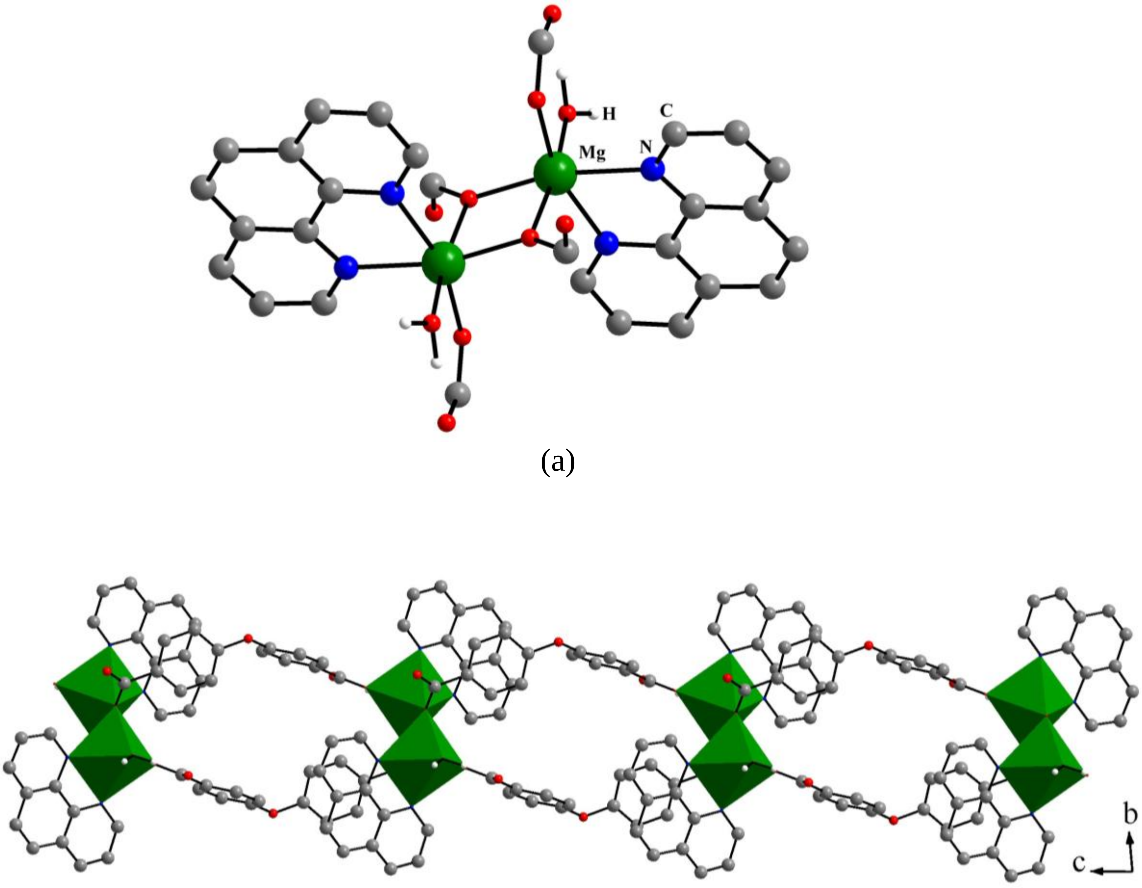
Table 3: Selected Bond Angles (degree) observed in compound **I**.

Bond	Angles (degree)	Bond	Angle (degree)
O(3)-Mg(1)-O(1)	88.20(7)	O(2)-Mg(1)-N(2)	96.44(7)
O(3)-Mg(1)-O(2)	102.04(7)	O(2)#1-Mg(1)-N(2)	92.25(7)
O(1)-Mg(1)-O(2)	92.79(7)	O(3)-Mg(1)-N(1)	87.72(7)
O(3)-Mg(1)-O(2)#1	93.73(7)	O(1)-Mg(1)-N(1)	96.47(8)
O(1)-Mg(1)-O(2)#1	171.11(7)	O(2)-Mg(1)-N(1)	166.76(7)
O(2)-Mg(1)-O(2)#1	78.32(7)	O(2)#1-Mg(1)-N(1)	92.27(7)
O(3)-Mg(1)-N(2)	161.37(7)	N(2)-Mg(1)-N(1)	100.11(6)
O(1)-Mg(1)-N(2)	88.60(7)		

Symmetry operation used to generate equivalent atoms for I: #1 –x, -y+1, -z+2

The bridging carboxylate oxygen atoms [O (2)] cause the formation of the building blocks of Mg_2O_2 cores (Figure 7a), in which the Mg···Mg distance is 3.222 Å and Mg–O–Mg angle is 101.6°. These cores are interconnected by OBA ligands into double-chain structures (Figure7b).

The coordinate water molecule and the presence of terminal C–O bonds in **I** gives rise to two types of significant O–H···O hydrogen bonds. The intra-molecular hydrogen bonding stabilized further the one-dimensional structures and the inter-molecular hydrogen bonding extended the structures in the two-dimension (Figure 8). It is important to mention that the pattern of intra- and inter- molecular hydrogen in **I** is comparable with the α-helix and β-sheet structure of DNA. In addition to these, very weak C–H···O hydrogen bonds have also been observed. A complete list of these interactions is given in table 4.



(a)

(b)

Figure. 7 (a) The structure of Mg_2O_2 core within $Mg_2O_6N_2$ dimer in **I**, (b) The one-dimensional connectivity in **I**.

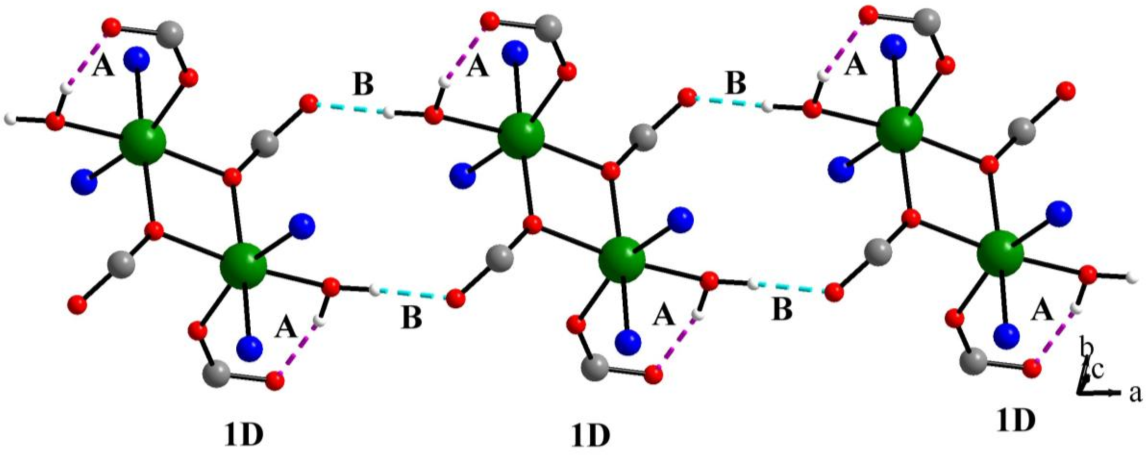


Figure 8: The intra-molecular (denoted as A) and inter-molecular (denoted as B) observed in **I**. Note the formation of two-dimensional supra-molecular structure though the hydrogen bonding between the one-dimensional motifs.

Table 4: Hydrogen bond interactions in compound **I**.

D □ H···A	D □ H	H···A	D···A	D □ H··A
O(1) □ H(1A)··O(4)	0.94(2)	1.78(2)	2.684(3)	161(3)
O(1) □ H(1B)··O(5)	0.94(2)	1.84(2)	2.767(2)	173(2)
C(3) □ H(3)··O(3)	0.93	2.53	3.454(3)	174
C(16) □ H(16)··O(5)	0.93	2.46	3.311(3)	152

The arrangement of the aromatic organic ligands (OBA and 1,10-phenathroline) indicate that the favorable π···π interactions between the ligand molecules play an important role in the formation and stability of the compound (Figure 9). The role of π···π interactions in the stability of lower dimensional structures in metal-organic coordination polymers has been a topic of much interest. In the present compound inter-molecular π···π interactions involving the 1,10-phenanthroline and intra-molecular π···π interactions involving OBA and 1,10-phenanthroline ligands are observed (Figure 10).

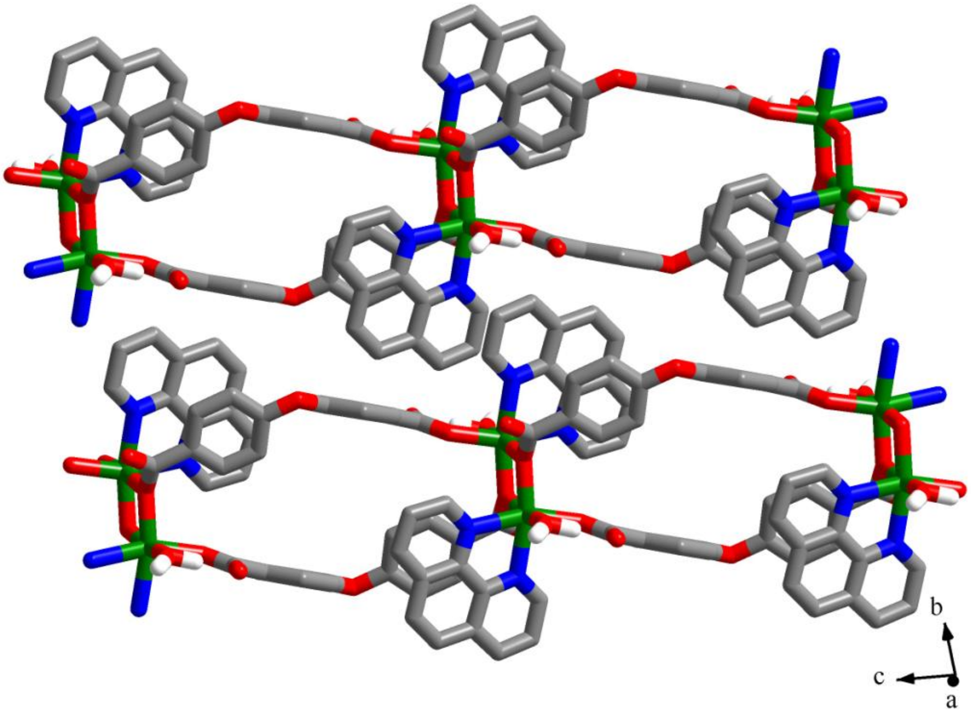
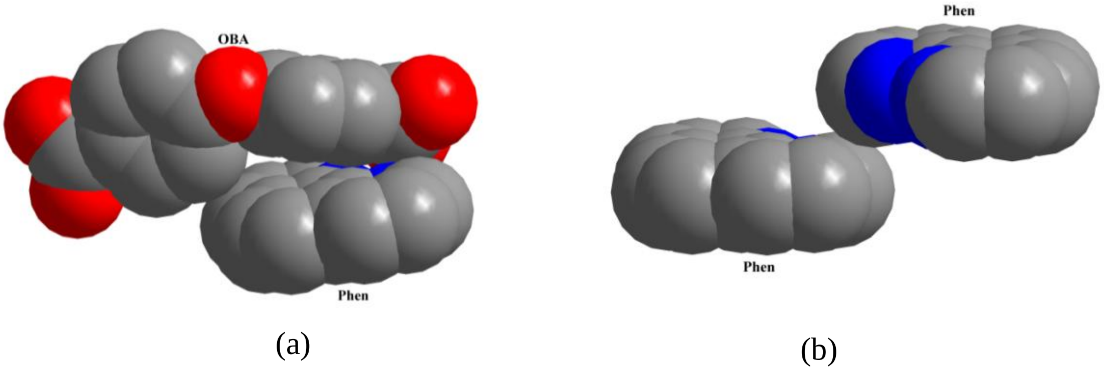


Figure 9: The arrangement of two one-dimensional structures showing the favourable π···π interactions in **I**.



(a) (b)

Figure 10: (a) The arrangement of 4,4’-oxybis(benzoate) (OBA) and 1,10-phenthroline (phen) which show intra-molecular π···π interactions, (b) The arrangement of two 1, 10-phenamthroline show inter-molecular π···π interactions.

From the figure 10a, it is clear that the two 1,10-phenanthroline rings are arranged anti-parallel to each other. This type of anti-parallel arrangement of aromatic rings is commonly observed in systems exhibiting dipolar properties.

Both the hydrogen bonds and π-π stacking interactions result in the formation of a 3D supramolecular network.

Powder X-ray diffraction

The powder X-ray diffraction (XRD) patterns were recorded on crushed single crystals in the 2θ range 5- 50° by using CuKα radiation. The simulated XRD generated from the single-crystal studies and experimental PXRD patterns of compound **I** is given in figure 11. The XRD patterns of the as-synthesized compound was entirely consistent with the simulated XRD generated from the single-crystal studies. This indicates that the hydrothermally synthesized products are pure.

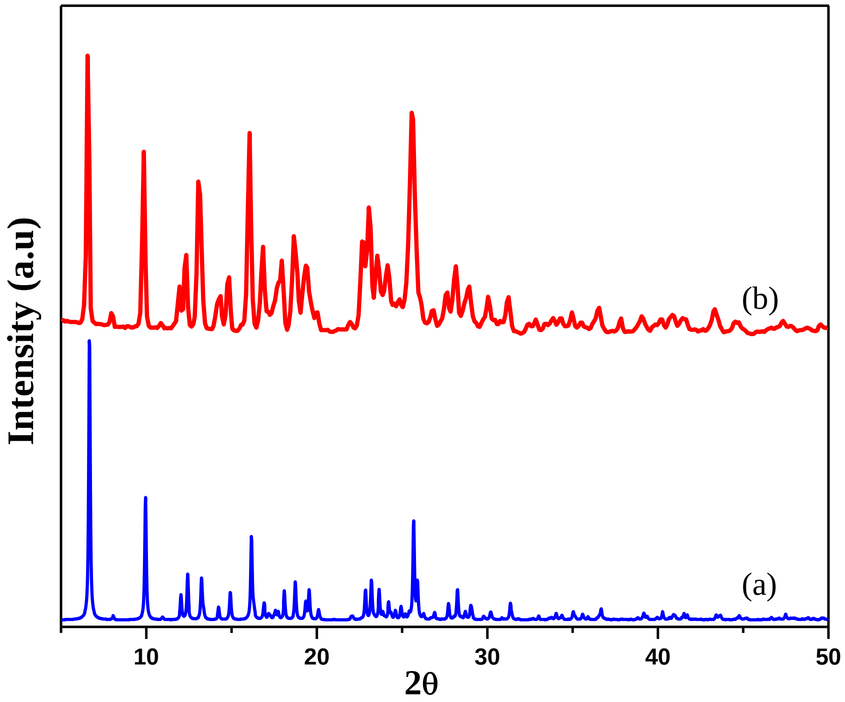


Figure 11: Powder XRD pattern for **I**: (a) simulated and (b) experimental.

Materials and Methods

Materials.

The reagents needed for the synthesis are $MgSO_4.7H_2O$ [Ranbaxy (India), 98%], 1,10’-phenanthroline [CDH(India), 98%], 4,4′-oxybis(benzoic acid) [Alfa Aesar, (India), 99%], and NaOH [CDH (India), 98%]. The water used was double distilled through a Millipore membrane.

Synthesis.

Compounds **I** was synthesized under hydrothermal conditions. In a typical synthesis, for **I**, $MgSO_4.7H_2O$(0.246 g, 1 mM) was dissolved in 8 ml of water. To this, 4,4′-oxybis(benzoic acid) (0.258 g, 1 mM), 1,10’-phenanthroline(0.198 g, 2mM) and NaOH (0.08 g, 2 mM) were added under continuous stirring. The mixture was homogenized for 30 min at room temperature. The final mixture was then sealed in a 23 ml PTFE lined autoclave and heated at 80 °C for 24 hours under autogenous pressure. The initial pH of the reaction mixture was 5, and there was no change in pH after the reaction. The final product, containing colourless needle like crystals, was filtered and washed with deionised water under a vacuum, and dried at ambient conditions (yield 80% based on Mg).

Single Crystal X-ray diffraction.

The single crystal structure of compound **I** was determined using a Siemens smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoK_α radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. The diffractometer operates on a PLATFORM – three-circle goniometer for precision movement of the crystal in ω and φ plus an automatic 2θ range for the detector and a two-dimensional Charge-coupled Device (CCD) detector with a 9 cm diameter input imaging area.

Powder X-ray diffraction.

The powder X-ray diffraction patterns of compound **I** was recorded on a Philips X’pert Pro X-ray powder diffractometer, using a flat plate sample holder. The incident X-ray is monochromatic and based on CuK_α. The detector is a liq. N_2 cooled solid state detector or a simple scintillation counter.

Conclusion

- We have hydrothermally synthesized a new metal-organic network compound using 4, 4’-oxybis (benzoic acid), 1, 10-phenthroline and magnesium salt.
- The products have been obtained as colourless needle like crystals.
- We have determined the structure of the synthesized compound using single crystal diffraction.
- The compound has one-dimensional connectivity and it form three dimensional supramolecular structure through the hydrogen bonding and $\pi\cdots\pi$ interactions.
- The powder X-ray diffraction studies on the crushed single crystals have performed and it confirmed that the compound has been obtained as pure phase.

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