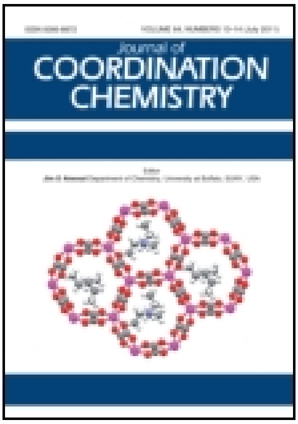

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and spectroscopic characterization of Mn(II) doped organic amine templated chlorocadmiumphosphate $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals

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To cite this article: CH. Rama Krishna , U.S. Udayachandran Thampy , D.V. Sathish , CH. Venkata Reddy , A.V. Chandrasekhar , Y.P. Reddy , P.S. RAO & R.V.S.S.N. Ravikumar (2011) Synthesis and spectroscopic characterization of Mn(II) doped organic amine templated chlorocadmiumphosphate $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals, Journal of Coordination Chemistry, 64:24, 4276-4285, DOI: 10.1080/00958972.2011.638376

To link to this article: http://dx.doi.org/10.1080/00958972.2011.638376

Journal of Coordination Chemistry
Vol. 64, No. 24, 20 December 2011, 4276–4285

Synthesis and spectroscopic characterization of Mn(II) doped organic amine templated chlorocadmiumphosphate $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals

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(*Received 8 July 2011; in final form 26 October 2011*)

Chlorocadmiumphosphate $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals doped with Mn(II) are grown at room temperature *via* organic amine template method and characterized by spectroscopic techniques to obtain information on the nature of the incorporated Mn(II). Powder X-ray diffraction patterns of the sample are indexed to monoclinic cell and average crystalline size is found to be around 55 nm. The optical absorption spectrum exhibits various bands which are characteristic of Mn(II) in distorted octahedral site symmetry, confirmed by characteristic resonance signal at $g = 2.018$ observed in the EPR spectrum. Fourier transform infrared spectrum shows the specific vibrations of phosphate and organic molecules. Thermal curves indicate that the crystal is stable at 307°C; above this temperature crystal structure disintegrates due to removal of the organic amine template.

Keywords: Mn(II) doped $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals; Powder X-ray diffraction; Thermogravimetric analysis; Spectroscopic techniques; Octahedral site symmetry

1. Introduction

Microporous solids have attracted attention due to their rich structural chemistry and potential applications in ion exchange, separation, catalysis, etc. [1]. Since the discovery of aluminum phosphate (AlPO) molecular sieves in 1982 [2], a wide range of metals such as Ga, In, Sn, and transition metals (TMs) such as Zn, Fe, Co, Ti, Mn, Ni, Sc, V, and Mo have been incorporated into open-framework phosphates. Such materials are interesting for two primary reasons. First, the ability of some main group and TMs to form extended structures in three-, four-, five-, and six-coordinate environments implies that a large number of topologies can potentially be produced. Second, incorporation of TMs into phosphate-based frameworks offers the possibility of devising new materials

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2011.638376

with catalytic, magnetic, and photochemical properties associated with d-block elements. Generally, these materials have been synthesized under hydrothermal conditions, particularly in the presence of organic amines as templates to direct the formation of particular structures. In very few cases, such organic amines are attached to the metal centers as ligands [3–7]. The synthesis of open-framework cadmium phosphates is a particularly unexplored area, although many condensed cadmium phosphates are known [8, 9].

Synthesis and structure of an open-framework cadmium phosphate, $K_4[Cd_3(HPO_4)^{4-}(H_2PO_4)^2]$, which has a layered structure was reported [10]. To the best of our knowledge, few organically templated cadmium phosphates have been reported [11–13]. Compounds of Mn(II/III) containing open-framework materials play vital and versatile roles in the redox biochemistry of many organisms. Manganese is the metal center in enzymes such as catalase, superoxidase, dismutase and an increased knowledge of their catalytic activity in oxidation processes can be advantageous [14–16].

Metal-containing frameworks are active catalysts in several reactions, so incorporation of TMs into these materials should provide more shape-selective options. The catalytic properties are mainly attributed to position and coordination of the TM ions in the molecular sieve framework. Therefore, characterization of transition metal states is a very important issue for study. For paramagnetic ions, spectroscopic techniques (UV-Vis absorption and electron paramagnetic resonance (EPR)) provide detailed information on the local environmental and nearby nuclei. Therefore, incorporation of TMs into the framework materials has attracted interest due to potential applications of such materials within heterogeneous catalysis [17, 18].

Recently we prepared chlorocadmiumphosphate crystals doped with TM ions, such as Cr(III), Co(II), and Fe(III) and spectrally characterized them to identify the nature of doped ions in the framework material. In these compounds the dopant ions exhibited distorted octahedral symmetry and partially covalent bonding with the ligands. The vibrational bands of phosphate and organic molecules are observed with slight changes in their wavenumbers [19–21].

In this work, Mn(II) is selected as a paramagnetic spin probe which is very sensitive to the local environment. The nature of manganese sites in 1,6-diaminohexane templated chlorocadmiumphosphate $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystalline material are studied by spectroscopic techniques.

2. Experimental

2.1. *Materials and synthesis*

1,6-Diaminohexane (DAH) ($C_6H_{16}N_2$) and cadmium chloride ($CdCl_2$) were purchased from Aldrich Corp.; phosphoric acid (H_3PO_4) and manganese chloride ($MnCl_2 \cdot 6H_2O$) were purchased from Merck Chemicals. All chemicals are of analytical pure grade and used as received.

Mn(II) doped chlorocadmiumphosphate $Cd(HPO_4)Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals are prepared by the following procedure. A mixture of 1.7 g of DAH is dissolved in water, to which 3.96 g of phosphoric acid is added. To this mixture, an aqueous solution containing 4 g of cadmium chloride is added dropwise under continuous stirring. The reaction can be written as follows:

$$\begin{aligned} &H_3PO_4 + 0.5NH_2(CH_2)_6NH_2 + \left(Cd^{2+}; 2Cl^-\right) \\ &\quad \rightarrow CdHPO_4Cl \cdot \left[H_3N(CH_2)_6NH_3\right]_{0.5} + HCl. \end{aligned}$$

Later, 0.1 mol % of manganese chloride is added separately. A light colored precipitate is obtained, which is completely dissolved by adding phosphoric acid. The solution on slow evaporation at room temperature yielded needle-shaped crystals of the complex, which are stable at normal conditions.

2.2. *Physical measurements*

The prepared crystalline material is characterized by powder X-ray diffraction (PXRD), thermal analysis and various spectroscopic techniques. Powder X-ray pattern of the sample is recorded on a PANalytical Expert Powder difractometer. Scherrer's equation is employed to estimate the primary crystalline size of the prepared crystals. The recorded powder diffraction data of the crystalline samples is indexed by POWD program of version 2.2. The weight loss and thermal behavior of the samples are investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) performed on a TA Instrument Q 600 SDT, 20 mg of prepared sample, heated at a rate of $10^\circ C\,min^{-1}$ from room temperature to 800°C. Fourier transform infrared (FT-IR) spectrum is recorded on a Thermo Nicolet 6700 FT-IR. The UV-Vis absorption spectrum of as prepared crystals is studied by using a JASCO V-670 spectrophotometer from 300to 650 nm. Polycrystalline EPR spectrum is recorded on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies having a 100 kHz field modulation.

3. Results and discussion

3.1. *PXRD studies*

The PXRD patterns of Mn(II) doped $CdHPO_4Cl\cdot[H_3N(CH_2)_6NH_3]_{0.5}$ crystals are shown in figure 1, with narrow reflections indicative of highly crystalline nature. It contains many intense diffraction peaks between 6° and 25° of 2θ as usually observed for inorganic microporous solids [22]. In the diffractograms, the peak very close to $2\theta = 10^\circ$ exhibits a stronger intensity than any other peak (see figure 1). This is characteristic of layered compounds [23]. The average crystalline size was evaluated from Scherrer's formula with full-width at half-maximum (FWHM) intensity. The calculated value of crystalline size is 55 nm, which confirmed the nanosize of the prepared material. The diffraction patterns are indexed to a monoclinic unit cell with the lattice parameters $a = 1.1286$, $b = 1.4738$, $c = 1.1595$ nm; $\beta = 92.105^\circ$ and cell volume as $V = 1.92743$ $(nm)^3$. The calculated parameters are given in table 1.

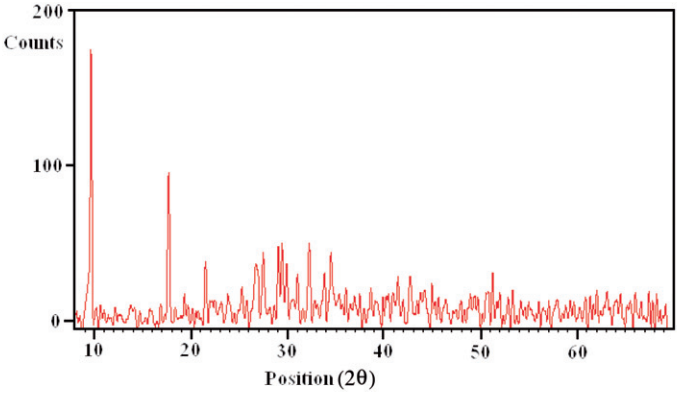

Figure 1. PXRD pattern of Mn(II) doped chlorocadmiumphosphate crystals.

3.2. *TG-DTA studies*

Thermal behavior studies of Mn(II) doped $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals (figure 2) by TG-DTA and DSC analysis show the existence of several transformations with and without weight loss. Generally below 300°C, the decomposition curves reveal a loss of mass, which can be attributed to adsorbed water in the compound, or to the existence of water in the cavities partially occupied by hexane diammonium cations.

When the sample is heated from room temperature to 800°C, it loses nearly 23% of weight and the weight loss cannot be observed above 380°C. In the present case, two-step weight losses can be clearly observed at 106–180°C and 180–485°C for Mn(II) doped $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals. The initial step with endothermic effect corresponds to removal of physically adsorbed water and the second one with a strongly exothermic process is due to the combustion decomposition of template [24]. The DTA curve shows a first significant endothermic peak at 160°C, followed by a series of endothermic peaks from 307°C to 380°C. The TGA curve shows an important weight loss corresponding to these peaks, which can be assigned to removal of water from condensation of two $H_2PO_4^-$ anions and decomposition of the organic entities. This decomposition leads, at the end of the experiment, to a consistent viscous residue of polyphosphoric acids and carbon black. The structure of the crystal system is stable at 307°C but after that it immediately decomposes due to the removal of DAH organic template. Above this temperature, two endothermic peaks at 572°C and 742°C are present, which may be due to weight loss in the combustion and complete removal of the organic fragments from this material. This trend follows the type of layered materials and is consistent with the previously reported similar materials [25–27].

3.3. *FT-IR studies*

Figure 3 shows the FT-IR spectrum of Mn(II) doped $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals. The closeness of the FT-IR bands is due to the existence of hydrogen bonds of fixed strengths in the crystal. Generally, the free PO_4^{3-} tetrahedron with an ideal T_d symmetry has four vibrational modes: the non-degenerate symmetric stretching mode ν_1, the doubly degenerate bending mode ν_2, the triply asymmetric stretching mode ν_3,

Table 1. PXRD investigations of Mn(II) doped chlorocadmiumphosphate $CdHPO_4Cl \cdot (H_3N(CH_2)_6NH_3)_{0.5}$ crystals.

d-spacing (Å)		Int.	Indices			2*θ* (°)	
Observed	Calcd	Observed	*h*	*k*	*l*	Observed	Calcd
14.738	14.738	30	0	1	0	5.99	5.99
11.279	11.279	6.3	2	0	0	7.83	7.83
9.110	9.110	100	1	0	1	9.70	9.70
4.999	4.999	85	0	0	2	17.73	17.73
4.571	4.586	7.5	−2	0	2	19.40	19.34
4.123	4.126	10	−5	0	1	21.53	21.52
3.730	3.724	8.3	4	0	2	23.83	23.87
3.529	3.530	7.4	−6	0	1	25.21	25.21
3.335	3.334	17	5	0	2	26.71	26.71
3.240	3.252	21	5	1	2	27.51	27.40
3.072	3.075	39	−7	0	1	29.04	29.01
3.033	3.038	26	5	2	2	29.42	29.38
2.985	2.985	35	−4	3	2	29.91	29.91
2.880	2.872	24	−2	4	2	31.03	31.11
2.773	2.772	22	6	2	2	32.25	32.27
2.718	2.720	9.6	−7	0	2	32.93	32.90
2.646	2.644	17	3	5	1	33.85	33.87
2.597	2.597	31	7	3	1	34.51	34.51
2.538	2.539	10	0	5	2	35.33	35.32
2.432	2.432	5.6	−8	1	2	36.93	36.93
2.328	2.333	13	2	6	1	38.64	38.56
2.293	2.304	2.4	9	2	1	39.26	39.05
2.237	2.239	2.7	8	4	0	40.28	40.24
2.182	2.182	12	8	4	1	41.34	41.35
2.063	2.063	6.8	−10	0	2	43.85	43.84
2.012	2.012	6.4	6	6	1	45.02	45.01
1.989	1.990	8.8	7	5	2	45.57	45.54
1.953	1.954	5.2	7	6	0	46.46	46.44
1.933	1.933	6.7	1	7	2	46.97	46.98
1.803	1.805	5.1	6	7	1	50.58	50.51
1.783	1.784	6.3	−5	7	2	51.19	51.13
1.592	1.592	2.4	−12	4	2	57.87	57.89
1.554	1.554	4.8	−4	9	1	59.43	59.42

$a = 2.2559$ nm, $b = 1.4738$ nm, $c = 0.9998$ nm; $\beta = 90.52°$, and $V = 3.3241$ $(nm)^3$.

and the triply degenerate asymmetric bending mode ν_4. All the modes are Raman active, whereas only ν_3 and ν_4 are active in the FT-IR. Localization of two protons to PO_4^{3-} reduces the symmetry from T_d to C_{2V}. With its crystalline environment in the studied compound, the $H_2PO_4^-$ anion occupies a site of lower symmetry, C_1. The reduction from T_d symmetry of the PO_4^{3-} leads to a splitting of the degenerate FT-IR modes and to the activation of the inactive ones.

The absorption bands observed at 400–700 cm^{-1} and 900–1250 cm^{-1} are all assigned to various vibration modes of PO_4^{3-} [28, 29]. The band of average intensity at 803 cm^{-1} corresponds to P–O(H) stretching in HPO_4^{2-} groups [30, 31]. The presence of water is confirmed by its OH_2 bending and stretching vibrations. Bands at 1650 and 3175 cm^{-1} are, respectively, attributed to water bending and stretching motions [32]. From the spectrum it is clear that the organic groups are also present and are assigned as follows, a broad band extending from 3400 cm^{-1} to 2500 cm^{-1} is due to symmetric and asymmetric stretching modes of NH_3, NH, CH, and OH. Frequencies at

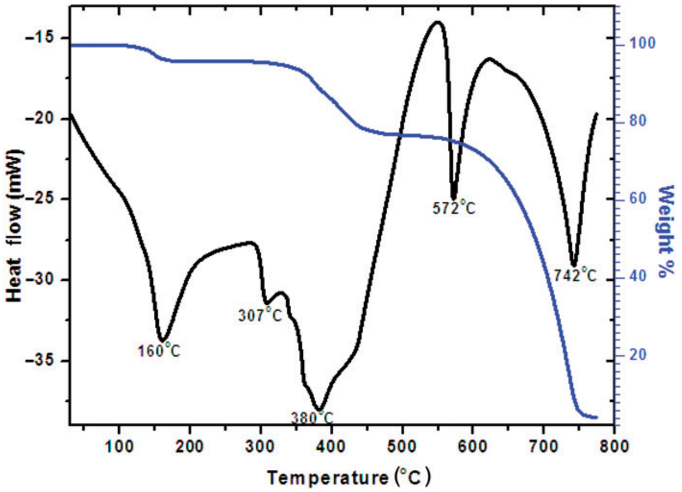

Figure 2. TGA–DTA curves of Mn(II) doped chlorocadmiumphosphate crystals.

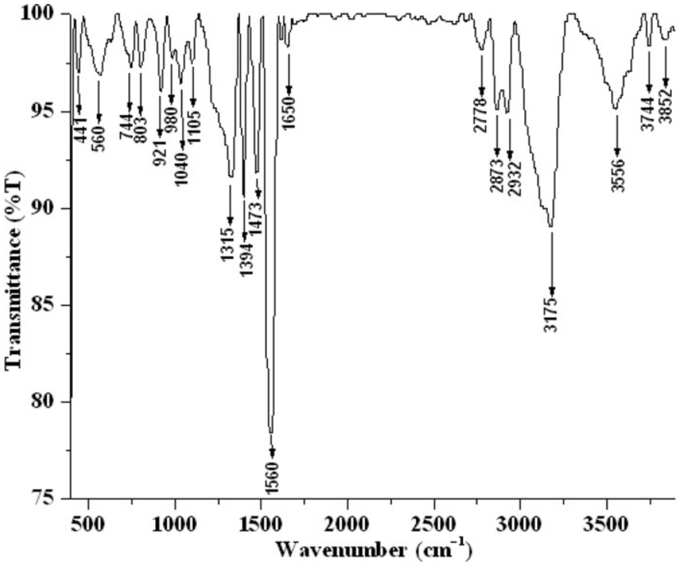

Figure 3. FT-IR spectrum of Mn(II) doped chlorocadmiumphosphate crystals.

1700–1300 cm^{-1} are attributed to δ(NH), δ(CH), and δ(OH) bending modes [33]. These vibrational bands are observed due to DAH [25, 34]. The band at 1105 cm^{-1}, characteristic of all framework materials, can be assigned to asymmetric stretching vibrations of T–O–T and T–O–M [33, 34], where T stands for the central atom in the primary units as TO_4 tetrahedra. The corresponding symmetric vibration gives a peak close to 744 cm^{-1}. Moreover, the band near 441 cm^{-1} is ascribed to bending vibrations of T–O–T and T–O–M [35, 36]. The FT-IR spectrum of the prepared sample (figure 3)

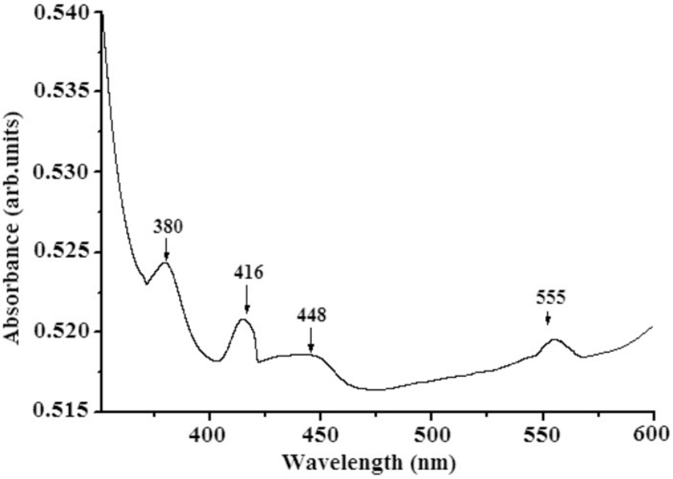

Figure 4. UV-Vis spectrum of Mn(II) doped chlorocadmiumphosphate crystals.

exhibits several O–H vibrations. Those observed at 3744 and 3852 cm^{-1} are assigned to H–O(P) stretching in HPO_4^{2-} ions [30]. All observed vibrational bands are in tune with similar compounds.

3.4. *UV-Vis absorption studies*

The formation of Mn(II) doped $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals is confirmed by UV-Vis spectra. The electronic absorption spectrum of prepared material from 200 to 600 nm is shown in figure 4. The spectrum shows various spin-forbidden d–d bands at 380, 416, 448, and 555 nm which are characteristics of octahedral site symmetry for Mn(II) ions in the framework material. The bands observed at 380, 448, and 555 nm depend on crystal field parameter Dq and are assigned to the transitions $^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$, $^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$, and $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, respectively; the band observed at 416 nm is assigned to the transition $^6A_{1g}(S) \rightarrow {}^4A_{1g}(G) + {}^4E_g(G)$, which is independent of D_q. The D_q and Racah parameters (B and C) have been calculated by fitting the experimental frequencies to an energy level diagram for an octahedral d^5 high spin system [37] with Tree's correction factor (for Mn(II), $\alpha = 76\,\mathrm{cm}^{-1}$). The values obtained are $D_q = 780$, $B = 655$, and $C = 3200\,\mathrm{cm}^{-1}$. These values are in the range usually found for octahedral Mn(II) compounds [38]. The band data along with the calculated values are tabulated in table 2. The position of these bands, the evaluated crystal field (Dq), and Racah parameters are similar to those obtained for various related Mn(II) containing open-framework materials [39–41].

3.5. *EPR studies*

As ^{55}Mn hyperfine interaction is large and very anisotropic in low-spin Mn(II) complexes, isotropic spectra tend to be poorly resolved and undiluted powders give very broad lines. EPR spectra of low-spin Mn(II) complexes have been elusive, in part

Table 2. Band-head data in optical absorption spectrum of Mn(II) doped chlorocadmiumphosphate $CdHPO_4Cl \cdot (H_3N(CH_2)_6NH_3)_{0.5}$ crystals.

	Band positions		
		Wavenumber (cm^{-1})	
Transitions from $^6A_{1g}(S) \rightarrow$	Wavelength (nm)	Observed	Calculated
$^4T_{1g}(G)$	555	18,031	18,078
$^4T_{2g}(G)$	448	22,315	21,562
$^4A_{1g}(G) + {}^4E_g(G)$	416	24,032	24,056
$^4T_{2g}(D)$	380	26,309	26,150

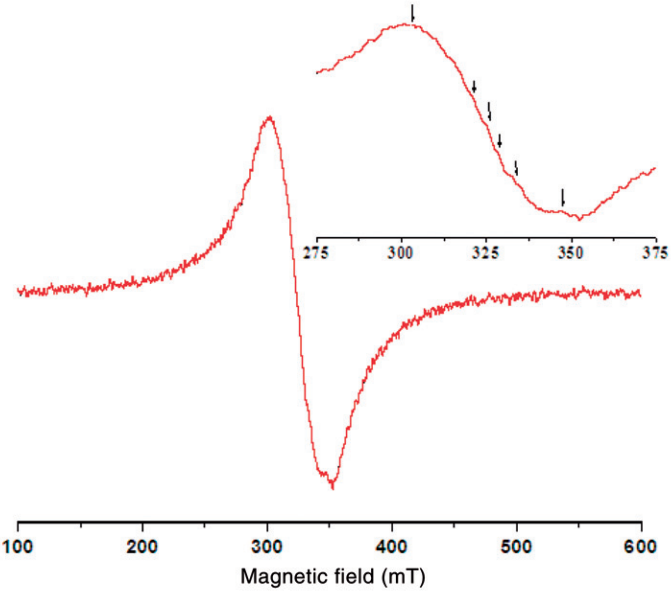

Figure 5. Polycrystalline EPR spectrum of Mn(II) doped chlorocadmiumphosphate crystals ($\upsilon = 9.15025$ GHz).

because of high-spin Mn(II) decomposition products which have easily observed spectra. A typical polycrystalline X-band ESR spectrum, observed at room temperature for Mn(II) doped $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals, is shown in figure 5, which has six hyperfine lines centered around $g = 2.018$, characteristic of octahedral site symmetry of Mn(II) within the framework material with an average hyperfine splitting constant $A = 100.9\,cm^{-1}$. These ESR parameters indicate that this Mn(II) species has octahedral coordination, consistent with other related compounds, consistent with an extra-framework position [42–44]. In general, the *g*-value for the hyperfine splitting is indicative of the nature of the bonding. If the *g*-value shows a negative shift with respect to the free electron value (2.0023) then the bonding is ionic and, conversely, if the shift is positive, then the bonding is more covalent. In the present case, the *g*-value shows positive shift (0.01558), indicative of covalent bonding between Mn(II) and ligands.

The sextet lines of Mn(II) species in this framework material are not well-resolved and unequal in spacing (inset of figure 5). This can be explained by the spin Hamiltonian [45, 46]. For Mn(II) with electron spin $S = 5/2$, there are five different $\Delta_M = 1$ transitions, where M is the electron spin quantum number. For an isotropic g factor, the transitions other than $\Delta_M = +1/2 \rightarrow -1/2$ strongly depend on the orientation with respect to the magnetic field and are typically not observed in powder samples. The $\Delta_M = +1/2 \rightarrow -1/2$ transition is split into a sextet by the hyperfine splitting A of the manganese nuclear spin $I = 5/2$. The $+1/2$, $m \rightarrow 1/2$, m transitions with $\Delta_m = 0$, where m is the nuclear spin quantum number, are allowed transitions which give a sextet spectrum and the $\Delta_M = 1$, $\Delta_m = 1$ transitions are forbidden transitions which show weak lines between the lines of the sextet for immobile Mn(II) ions. Figure 5 reflects this case. The second-order terms involving the hyperfine splitting and the zero-field splitting cause the allowed transitions to shift and broaden, dependent on m. They become broader and spaced further apart at high field. This is the reason why the splittings of the sextet in figure 5 are unequal, which suggests significant zero-field interactions. An average hyperfine splitting A is obtained by averaging the five separations between successive hyperfine lines and in the present case the value is $100\,\mathrm{cm}^{-1}$. The results obtained agree with those of related Mn(II) incorporated open-framework materials.

4. Conclusions

On the basis of the results, we conclude that a hybrid material Mn(II) doped $CdHPO_4Cl \cdot [H_3N(CH_2)_6NH_3]_{0.5}$ crystals has been synthesized at room temperature using DAH as the structure-directing agent. The framework structure of this material was characterized by PXRD. UV-Visible studies gave bands characteristic of Mn(II), primarily as distorted octahedral site symmetry. These studies are supported by EPR spectrum which shows the resonance signal at $g = 2.0179$ exists at hydrated extra-framework positions as distorted octahedral Mn(II). FT-IR studies confirm possible vibrational bands related to DAH as well as tetrahedral phosphate. The template role played by DAH for the synthesis of this layered material could direct rational design of other layered topologies by using organic molecules as structure directing agents in the synthesis. TGA and DTA curves from thermal analysis demonstrated that the crystal structure collapses whenever DAH is removed.

Acknowledgments

RVSSN thanks the University Grants Commission, Government of India, New Delhi for sanctioning UGC-DRS to the Department of Physics, ANU to carry out this research work.

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