

# Synthesis, Characterization and Magnetic Properties of Nanocomposite Pb<sub>2</sub>MnO<sub>4</sub> and PbO: A New Metal-Organic Complex

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A new paramagnetic nanocomposite of  $Pb_2MnO_4$  and PbO was synthesized by thermal decomposition of new metal-organic complex formulated as  $[Mn(H_2O)_6][Pb(dipic)_2]\cdot 2H_2O$  (1) (dipic = pyridine-2,6-dicarboxylic acid). The complex was characterized by atomic absorption, conductivity measurement, elemental analysis, Fourier transform infrared spectroscopy and ultra violet-visible spectroscopy. Thermal behaviour of complex 1 was studied by thermogravimetric analysis and differential scanning calorimetry. The complex 1 used as a precursor for preparation paramagnetic nanoparticles of  $Pb_2MnO_4$  and PbO by thermal decomposition method at 600 °C. These nanoparticles were characterized by FT-IR and X-ray diffraction and scanning electron microscopy. The magnetic behaviour of nanoparticles was studied using vibration sample magnetometer at room temperature.

Keywords: Bimetallic complex, Thermal decomposition, Paramagnetic behaviour, Mixed-oxide nanoparticles.

# **INTRODUCTION**

Many compounds of  $AB_2X_4$  family, in particular oxides (X = O), crystallize atambient conditions in the spinel structure. In spinels, A and B can be divalent, trivalent or tetravalent cations. In the normal pattern, the oxygen form a cubic close packed (face centred) array A(II) and the B(III) in tetrahedral (1/8 occupied) and octahedral (1/2 occupied) sites in the lattice. In the nanocomposite of Pb<sub>2</sub>MnO<sub>4</sub> that have spinel structure, the combination of Pb and Mn cations are very interesting as they may display concomitant and coupled dielectric and magnetic orders. In the cation of Pb<sup>2+</sup> lone-pair may induce polar distortions that couple charge and spin orders. Lead oxide, is one of semiconductor nanostructures, has important applications in storage batteries, glass industry and pigments [1].

Recently, nanocomposite has been proved as a promising option in order to improve mechanical properties. Nanocomposites exhibit a wide range of properties, including optical, electrical, catalytic [2] and biological activity [3], which is different from that of their bulk materials. Many chemical methods can be used for synthesis of magnetic nanocomposite such as, micro-emulsions [4], sol-gel syntheses [5], sonochemical

reactions [6], hydrothermal reactions [7], hydrolysis and thermolysis of precursors [8], flow injection syntheses, electrospray syntheses, etc. Magnetic nanoparticles have been explored for many applications, such as catalysts for water splitting [9-11], nanomedicine [12-14] as matrices for matrix-assisted laser desorption/ionization (MALD) analysis, heavily explored for biomedical applications, such as drug delivery, cancer therapy by magnetic hyperthermia, as contrast agents for magnetic resonance imaging (MRI) and the emerging technique of magnetic particle imaging (MPI) [15-17]. High surface area to volume ratio in nanoparticles, resulting in appearance of new properties in chemical, mechanical, electrical, optical, magnetic, electrooptical and magneto-optical properties of the nanoparticles that are different from their bulk properties. Using metal organic complex is a suitable method to produce metal oxides nanoparticles [18-20]. The thermal decomposition of metal organic complex causes the formation of smaller particles with high surface area. In the present work, complex of [Mn(H<sub>2</sub>O)<sub>6</sub>]-[Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O was synthesized and used as a precursor for preparation paramagnetic nanoparticles of PbO and Pb<sub>2</sub>MnO<sub>4</sub> by thermal decomposition of complex at 600 °C.

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# **EXPERIMENTAL**

All the chemicals used in the present study were commercially available with analytical grade of purity and used without further purification. Measurements C, H and N of complex were applied using a Pakin-Elmer 2400 CHN elemental analyzer. Atomic absorption spectroscopy on metals was performed using a Varian AA50 equipment. Molar conductivity measurement was recorded by Ciba Corning model check-mate 90 conductometer at room temperature. FT-IR spectra were recorded as KBr pellets on a FT-IR Perrin spectrophotometer. UV-Vis spectroscopy was done on a JASCO 7850 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was used for investigation the weight changes of inorganic complex simultaneously by TGA-PL equipment with heating rate 10 °C/min. The morphology of nanoparticles wasstudied by scanning electron microscopy technique (SEM) using a VEGA\\TESCAN-XMU. The XRD pattern of nanoparticles was conducted with X-ray diffractometer model X/-Pert MPD with monochromatized CuK $\alpha$  radiation. Magnetic properties of nanoparticles were studied at room temperature with applied magnetic fields up to 100000e which used to measure the magnetic properties of nanoparticles with vibrating sample magnetometer (VSM).

**Synthesis of [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O complex:** To synthesize the complex of [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O, an aqueous solution containing 5 mL of Pb(NO<sub>3</sub>)<sub>2</sub> (0.50 mmol)] was added to a suspension of pyridine 2,6-dicarboxylic acid (dipic) (167 mg, 1.0 mmol). The protons of dipic ligands are eliminated by an aqueous solution of NaOH (80 mg, 2.0 mmol, 2.0 mL) with continuous stirring at room temperature for 1 h. Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol) was dissolved in 10 mL of H<sub>2</sub>O and stirred for 1 h, was added to the above solution. The resulting solution was stirred at room temperature for 2h. Solution filtered off and left to evaporate in a beaker in air at room temperature for [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O are formed. m.p. 212 °C. Elemental analysis: Calcd. (found) % for C<sub>14</sub>H<sub>22</sub>O<sub>16</sub>N<sub>2</sub>PbMn: C: 22.81 (22.78), H: 2.98 (2.96), N: 3.80 (3.83).

**Preparation of nanocomposite Pb<sub>2</sub>MnO<sub>4</sub> and PbO:** The complex of  $[Mn(H_2O)_6][Pb(dipic)_2] \cdot 2H_2O$  were placed in the electric furnaces for 4 h in normal atmosphere and calcified at 600 °C in order to yield nanoparticles.

#### **RESULTS AND DISCUSSION**

The molecular structure complex of  $[Mn(H_2O)_6][Pb(dipic)_2]$ ·2H<sub>2</sub>O is shown in **Scheme-I**. The two deprotonated of dipicolinate, as tridentate chelating ligands are coordinated to Pb(II) and six molecular of water as terminal ligands are coordinated to Mn(II) center. Both metal centers have octahedral geometry.

Atomic absorption analysis was performed on the solution of complex and confirmed the existence of equal molar ratios of two metals in the structures of complex. The molar conductance is a colligative term so it directly depends on the number of ions in the complex solution, and is independent of the nature and size of ions. Therefore, a solution of inorganic complex in distillate water  $(10^{-4} \text{ M})$  was made and measured at room temperature by conductometer. The results show that the molar conductivity



Scheme-I: Schematic representation of [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O

of  $[Mn(H_2O)_6][Pb(dipic)_2]\cdot 2H_2O$  is 118 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in distilled water indicating the presence two ions in the structure of complex is confirmed. According to the reference, conductance of 100-131 cm<sup>2</sup>/ $\Omega$ .mol indicates bivalent electrolyte [21].

FT-IR spectrum of this complex is shown in Fig. 1, which confirms the presentation and coordination of ligands to metal centers. The main characteristic peaks of this complex are assigned. Strong and broad absorption bands at wavenumbers 3589-3334 cm<sup>-1</sup> are attributed to stretching v(OH) of coordinated and lattice water molecules. Other bands in 1615 cm<sup>-1</sup> is attributed to  $v_{as}$ (COO) of dipicolinate groups and bands in 1421, 1384 and 1270 cm<sup>-1</sup> are due to  $v_{s}$ (COO) vibration. In this complex the value of  $\Delta v$  is 194 cm<sup>-1</sup> indicating that carboxylate group is coordinated as monodent to the central atom. The weak band at 610 cm<sup>-1</sup> is assigned to Ni-N stretching vibration in complex [22-24].



Fig. 1. FT-IR spectrum of [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O

Fig. 2 shows the electronic spectrum of  $[Mn(H_2O)_6]$ -[Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O in H<sub>2</sub>O solvent. According spectrochemical series, dipic is a weak ligand [2,3]. The electronic configuration of Pb<sup>2+</sup> is: [Xe]6s<sup>2</sup>4f<sup>45</sup>5d<sup>10</sup>, therefore, there is no electron transfer for this center. The electronic configuration of Mn<sup>2+</sup> is d<sup>5</sup> high spin, so *d*-*d* electron transfer of this center is spin forbidden. Two absorption bands at 190, 237 nm are detected to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  intra-ligand electron transfer of dipic ligand, respectively.





Fig. 3 shows TGA and DSC curves of  $[Mn(H_2O)_6]$ -[Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O. Thermogravimetric curve shows two weight loss peak, the first peak starting at 40 °C and continuing to 260 °C is due to the removal of crystallization and coordination water molecules. The second weight loss peak at 300-420 °C is related to the oxidation of dipic ligands. At this stage metal oxides are formed. The DSC results is consistent with TGA result and shows three peaks, the first endothermic peak at around 60-120 °C is related to the loss of crystallization water molecules and the second peak in the range 160- 200 °C is attributed to the coordination water molecules. A large exothermic peak at 400 to 580 °C is related to the burning of dipic ligands.

After calcination of  $[Mn(H_2O)_6][Pb(dipic)_2]\cdot 2H_2O$  in 600 °C for 4 h, nanopowder was performed. FT-IR spectrum of the nanoparticles is shown in Fig. 4, which confirms the calcination of complex. The broad band at 3421 cm<sup>-1</sup> is assigned to O-H stretching mode of hydroxyl group of adsorbed water molecules. The bands at 700 and 900 cm<sup>-1</sup> are attributed to Pb-O and Mn-O stretching. The XRD pattern of nanoparticles is shown in Fig. 5. Two different phases of Pb<sub>2</sub>MnO<sub>4</sub> and PbO nanoparticles indexed in this pattern. The pattern agrees with Pb<sub>2</sub>MnO<sub>4</sub> (JCPDS No.: 36-0844) which crystallizes in the space group P-42<sub>1</sub>c. Other observed peaks were attributed to the presence of PbO (JCPDS number: 38-1477) which has lattices with the parameters of a = 5.4903(4) Å, b = 5.8920(4) Å, c = 4.7520(4) Å, Z = 4 in Pcam. The crystallite size of particles was found to be 32.4 nm, which was calculated by Debye-Scherrer equation (eqn. 1):

 $D_{c} = \frac{K\lambda}{\beta\cos\theta}$ 





Fig. 5. X-ray powder diffraction pattern of the oxide nano-nanoparticles

where  $\beta$  is the breadth of observed diffraction peak at its half intensity maximum, K is the shape factor, which takes the value of 0.9 and  $\lambda$  is the X-ray wavelength of source used in XRD (1.54 Å).

Figs. 6(a-b) show SEM micrographs obtained for the nanoparticles of  $Pb_2MnO_4$  and PbO and bulk of  $[Mn(H_2O)_6][Pb(dipic)_2]$ .  $2H_2O$ . It is clear from Fig. 6a that  $Pb_2MnO_4$  and PbO particles are well below the size of 100 nm. Fig. 6b shows bigger particles for inorganic complex (bulk). Also SEM images of samples show the crystallites nature for nanoparticles and inorganic complex. The hysteresis loop at room temperature shows the linear increase of magnetization with applied magnetic field, which confirms the paramagnetic behaviour of nanocomposite (Fig. 7).



Fig. 3. TGA and DSC curves of [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O



Fig. 6. SEM micrograph of metal oxide nanoparticles (a) and complex of [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O



Fig. 7. Magnetization curve of mixed oxides nanoparticles of  $Pb_2MnO_4$  and PbO nanoparticles at 298 K

#### Conclusion

The complex of [Mn(H<sub>2</sub>O)<sub>6</sub>][Pb(dipic)<sub>2</sub>]·2H<sub>2</sub>O was synthesized. Single crystals of this complex were characterized by various techniques such as FT-IR, UV-visible, atomic absorption, elemental analysis and conductivity measurements. The weight and heat changes of this complex were also investigated by TGA and DSC. This complex was used as a precursor for preparation nanoparticles of Pb<sub>2</sub>MnO<sub>4</sub> and PbO by thermal decomposition method and characterized by FTIR, SEM, XRD and TEM. Magnetic property of nanoparticles was studied at room temperature and showed that the nanoparticles have ferromagnetic behaviour.

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# **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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