



Research Article

Investigation of Gas Storage Properties of Metal Complexes Including Dicarboxylic Acid Moities

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Abstract

The metal complexes of dicarboxylic acid derivatives were synthesized and their gas-storage properties were characterized. Metal complexes displaying various metal-organic frameworks with 4,5-imidazole-dicarboxylic acid ligand (L) with Mo(III), W(VI), Ce (III), Sm (III), and Sn (IV) were synthesized in order to examine their gas adsorption properties. The porous complexes were characterized by elemental analysis, FT-IR, ¹H-NMR, spectroscopic methods and microanalysis. Investigation of the structures of these complexes indicates that gases are most probably occluded in homogeneous and linear micropores which are composed of micropore units surrounded by dicarboxylate bridges. Gas storage and adsorption properties of these complexes were investigated via BET measurements. Sorption property of H₂ and N₂ was performed at temperature of 298 K and pressure of 1 bar.

Keywords: dicarboxylic acid ligand, synthesis of metal complex, lanthanides and transition metals, hydrogen, gas storage

1. Introduction

In our country, renewable energy sources and storage of the produced energy are of great significance due to limited energy sources and the gradual decrease. In order to meet with success of energy demands, energy store as a gas is one of the best methods [1,2].

In recent years, the design, synthesis and study of properties of metal-organic frameworks (MOFs) have attracted the huge interest of scientific community. Porous metal-organic frameworks (MOFs), which consist of the inorganic building units (connectors), are bridged by organic ligands [3,4] At present, high porosity and high specific surface area of MOFs can lead to many potential applications in gas storage [5].

Dicarboxylates and derivatives “ligands” are one of the most important structures in inorganic-organic hybrid coordination chemistry. Because, these ligands are able to create various metal-organic framework structures due to high oxygen and nitrogen content which yield bond creation with metal ions in different ways [6-8]. Therefore, dicarboxylates are good constituents in design of metal-organic structures thanks to their rich coordination structures [3].

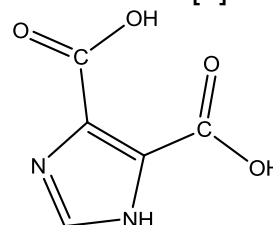


Figure 1. Imidazole dicarboxylic acid

In this study, 4,5-imidazole dicarboxylic acid was chosen as ligand (Figure 1.). This is due to multi-dentate bridged feature of these ligands in polymeric

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coordination chemistry and this efficient structure leads to exhibition of various coordination species.

2. Synthesis and Measurements

2.1. Synthesis of metal complexes

Various metal complexes were synthesised by using 4,5-Imidazole dicarboxylic acid and salts of transition metals (Mo and W), lanthanide group metals (Ce and Sm) or weak metal (Sn) (Figure 2.).

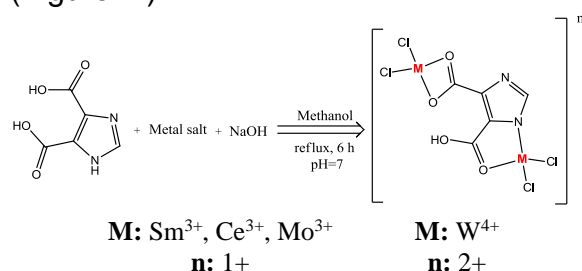


Figure 2. General synthesis methods of metal complexes

The structures of complexes were characterized by FT-IR, ¹H-NMR and elemental analysis.

L1Ce: IR (KBr, pelet, cm⁻¹) : 2972-2843 (COOH), 1578-1493 (C=O). ¹H NMR (600 MHz, DMSO, δ: ppm) : δ=12.7 (s, 2H, OH), 7.54 (s, H, CH=N), 3.39 (s, H, C-H). Elemental Analysis (%): C, 18.59; H, 1.59; N, 8.13.

L1Sm: IR (KBr, pelet, cm⁻¹) : 3336 (COOH), 1566(C=O). ¹H NMR (600 MHz, DMSO, δ: ppm) : δ=13.8 (s, 2H, OH), 7.67 (s, H, CH=N), 3.50 Elemental Analysis (%): C, 16,94; H, 1.92; N, 7.68.

L1W: IR (KBr, pelet, cm⁻¹) : 3130 (COOH), 1583 (C=O). ¹H NMR (600 MHz, DMSO, δ: ppm) : δ=12.7 (s, 2H, OH), 7.56 (s, H, CH=N), 3.41 (s, H, C-H) Elemental Analysis (%): C, 13,58; H, 1.24; N, 6.25.

L1Mo: IR (KBr, pelet, cm⁻¹) : 2972-2843 (COOH), 1577-1522 (C=O). ¹H NMR (600 MHz, DMSO, δ: ppm) : δ=12.7 (s, 2H, OH), 7.57 (s, H, CH=N), 3.40 (s, H, C-H) Elemental Analysis (%): C, 16,63; H, 1.37; N, 7.43.

L1Sn: IR (KBr, pelet, cm⁻¹) : 3043 (COOH), 1574-1538 (C=O). ¹H NMR (600 MHz, DMSO, δ: ppm) : δ=12.6 (s,

2H, OH), 7.55 (s, H, CH=N), 3.40 (s, H, C-H). Elemental Analysis (%): C, 29,65; H, 2.23; N, 13.72.

The molecular structure with 3D molecular network of complex L1Ce is shown in Figure 3.

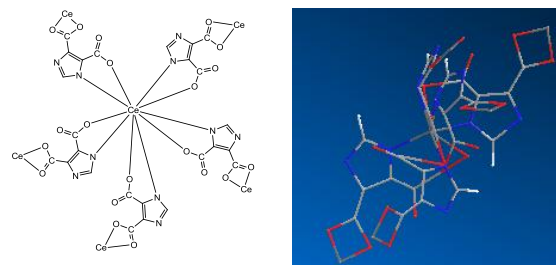


Figure 3. Molecular structure of L1Ce and 3D molecular network

2.2. Investigation of gas storage properties

Porous structure and gas adsorption capacities of synthesised complexes were examined by using BET (Surface Area Measurement Device). Adsorption isotherms of H₂ and N₂ gases were measured in 298 K and 1 bar (Table 1).

Table 1. Gas storage properties of synthesized complexes

Complexes	H ₂ storage (m ² /g)	N ₂ storage (m ² /g)	T (K)	P (bar)
L1Ce	89.26	52.26	298	1
L1Sm	120.32	90.33	298	1
L1W	43.68	18.54	298	1
L1Mo	35.30	11.92	298	1
L1Sn	32.70	10.13	298	1

3. Conclusions

The porous metal-organic frameworks (imidazole dicarboxylate complexes) has been successfully synthesized and characterized. Gas adsorption measurement showed that the pores of these complexes are suitable for nitrogen and hydrogen gases. Adsorption capacity of nitrogen is higher in comparison with other porous coordination polymers. It is also compared that H₂ storage capacities of the complexes synthesized in this work with other well-known nanoporous materials L1Sm has a better storage capacity than multi-walled carbon nanotubes under the same condition [9].

The results in this study clearly show that L1Ce and L1Sm exhibit higher N₂ and H₂ storage capacities due to their large pore sizes and much more the coordination numbers.

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4. References

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