

Proceedings of the 17th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 3–7, 2019

Magnetic Properties of Praseodymium-Organic Framework Containing H₂TPPS Ligand

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The presented work is focused on preparation and characterization of Metal-Organic Framework (MOF) with the chemical formula $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3] \cdot n\text{H}_2\text{O}\}_n$. This type of polymer was synthesized via hydrothermal reaction with $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and porphyrinic ligand H₂TPPS (where H₂TPPS = 4,4',4'',4'''-(porphine-5, 10, 15, 20-tetrayl)tetrakisbenzenesulfonate). Prepared MOF was characterized by single-crystal X-ray diffraction, infrared spectroscopy, thermal and elemental analysis, and the magnetic susceptibility measurement. The crystal structure of prepared MOF is formed from Pr(III) ions arranged in 1D chains bridged by four H₂TPPS ligands forming the final 3D framework with opening size $4.9 \times 10.4 \text{ \AA}^2$ and $9.7 \times 5.1 \text{ \AA}^2$, which are filled with water molecules. The magnetic properties of the coordination polymer were studied by magnetic susceptibility $\chi_M(T)$, and magnetization $M(H)$ measurements in an external dc field up to 7 T in the temperature range from 1.8 to 300 K. The experimental results revealed a significant reduction of the magnetic moment below 50 K as an evidence of the presence of low-lying quasi-doublet in the energy spectrum of Pr ion in $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3] \cdot n\text{H}_2\text{O}\}_n$.

DOI: [10.12693/APhysPolA.137.770](https://doi.org/10.12693/APhysPolA.137.770)

PACS/topics: praseodymium, porphyrine, metal-organic framework, magnetic properties, spin crossover

1. Introduction

Metal-organic frameworks (MOFs) represent a class of porous coordination polymer, consisting of periodically connected organic linkers and inorganic ions or ion clusters. Conveniently, connections of these building block lead to materials which have potential applications in various area, e.g., gas sorption and separation, drug delivery, catalysis, and magnetism [1]. Porphyrinic ligands are one of the very valuable linkers in the synthesis of MOFs. In fact, application porphyrinic ligands in design MOFs forms a new subsection of these porous polymers, known as Metaloporphyrinic frameworks (MPFs) [2]. Lanthanide ions as an inorganic node in the compound of MOFs have attracted extensive interest due to their versatile coordination numbers and a lot of unpaired electrons, being precursors of interesting, light-harvesting, fluorescent properties [3]. Special attention has been paid to magnetic properties of MOFs containing gadolinium ions [4, 5], however other rare-earth ions such as europium, holmium and cerium have also been investigated [6]. Very little work has been devoted to the magnetic properties of praseodymium ions contains MOFs. Herrero-Martín et al. [7] demonstrated unexpected magnetic behaviour in $(\text{Pr}_{0.7}\text{Sm}_{0.3})_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ when partial oxidation of Pr^{3+} into Pr^{4+} was observed, after crossing critical temperature T upon cooling. It was

emphasized that this phenomenon is more complex than a simple valence change since it also involves the development of a strong hybridization between Pr 4*f* and O 2*p* orbitals below the critical temperature.

Therefore, in this study, we present the results from the magnetic study (magnetisation and DC magnetic susceptibility) and structural properties of praseodymium ions incorporated into metaloporphyrinic frameworks. The objectives of this study are first to investigate the magnetic properties of Pr ions in MOFs.

2. Experimental

The porous coordination polymer $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3] \cdot n\text{H}_2\text{O}\}_n$, was prepared under autogenous pressure, using distilled water as a solvent in 45 ml Teflon autoclave.

The infrared spectrum was recorded on Avatar FT-IR 6700 spectrometer using KBr technique in the range of wavenumber 4000–400 cm^{-1} . Thermogravimetric analysis was performed in the temperature range 25–900 °C, with a heating rate of 9 K/min using anSTANetzsch 409-PC instrument. The single-crystal X-ray diffraction data set was measured on the Nonius Kappa CCD diffractometer equipped with a Bruker APEX II detector with Mo/ K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Magnetic properties were investigated using a SQUID (Superconducting Quantum Interference Device) magnetometer MPMS3 in the external dc fields up to 7 T and in the temperature range of 1.8–300 K. A powder sample was placed in a polypropylene VSM capsule to avoid the contribution of the sample holder. A core diamagnetic susceptibility estimated using experimental value for H₂TTP and Pascal's constants was subtracted from total susceptibility.

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3. Results and discussion

The crystal structure of complex polymer $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3] \cdot n\text{H}_2\text{O}\}_n$ is shown in Fig. 1a. The single-crystal X-ray diffraction study revealed that this complex polymer crystallizes in the tetragonal system with the space group P4/mcc, and asymmetric unit contains one Pr atom, two oxygen atoms, one sulfur atom, nine carbon atoms, and one nitrogen atom. H₂TPPS ligand in the title complex is 24-membered macrocyclic ring displays a totally planar configuration, the mean plane between four pyrrole rings and aryl rings is strict 90°. The neighboring porphyrin macrocyclic planes are parallel and the distance between them is 4.9835 Å, this pore is fulfilled with molecules of water, which was confirmed by infrared spectroscopy and thermogravimetric analysis. The Pr(III) is eight coordinated with the eight oxygen atoms from eight sulfonic ligands, this coordinated Pr(III) ion can be described as a square anti-prism coordination geometry, with the bond length Pr···O 2.438 Å, which is the normal range and comparable with those documented in the literature. The praseodymium ions with sulfonate group form a one-dimensional infinite $-\text{Pr}-(\text{SO}_3)_4-\text{Pr}-$ chain along the *c* crystallographic axis, with distance between Pr(III)···Pr(III) ions is 4.984 Å, see Fig 1c. Described coordination of eight Pr(III) ions to a molecule of H₂TPPS⁴⁻ ligand forming a condensed three-dimensional porous opening framework with the crystal water molecules residing in the voids, molecule of water is omitted for better viewing in Fig. 1. The framework contains three crossing cavities propagating along all crystallographic axes with sizes approximately $4.9 \times 10.4 \text{ \AA}^2$ and $9.7 \times 5.1 \text{ \AA}^2$, see Fig. 1b. Infrared spectroscopy confirmed the presence of lattice water in porous framework of the compound, likewise presence of adsorption bands of H₂TPPS ligand. Thermogravimetric analysis showed, that complex $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3] \cdot n\text{H}_2\text{O}\}_n$ undergoes the dehydration process after heating to 100 °C with the weight loss of 8% until 180 °C.

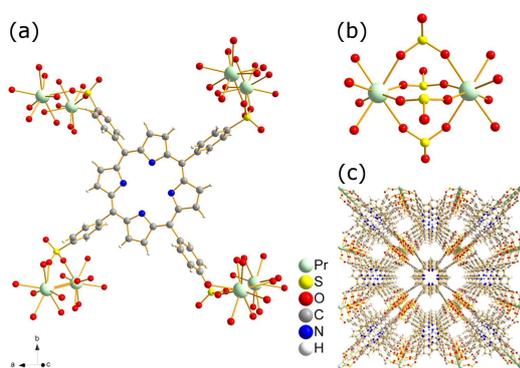


Fig. 1. (a) Coordination polymer $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3] \cdot n\text{H}_2\text{O}\}_n$, (b) 3D porous framework viewing along crystallographic axis, (c) cluster- $\text{Pr}-(\text{SO}_3)-\text{Pr}-$ with view bringing sulfonic group from H₂TPPS linker.

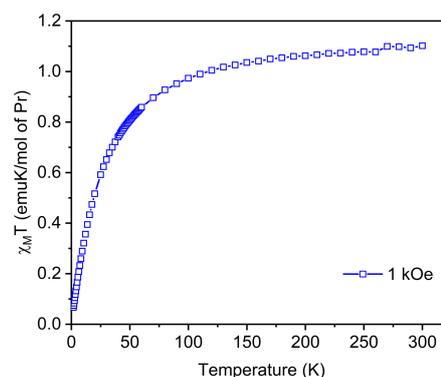


Fig. 2. Temperature dependence of molar magnetic susceptibility of $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3] \cdot n\text{H}_2\text{O}\}_n$.

The resulting dehydrated form $\{[\text{Pr}_4(\text{H}_2\text{TPPS})_3]\}_n$ is thermally stable up to 350 °C. There are two decomposition steps on TG above 350 °C, corresponding to the decomposition of organic linker. The final product of thermal decomposition was PrO₂.

To investigate the magnetic properties of the prepared MOF system, the molar magnetic susceptibility was measured in the range of 1.8–300 K under the external magnetic field of 1 kOe. Molar magnetic susceptibility was recorded in zero-field-cooled (ZFC) and field-cooled (FC) regimes, as shown in Fig. 2, but no irreversibility of the magnetic responses was observed. A gradual increase of the molar susceptibility was observed with the decreasing temperature.

In the temperature dependence of $(\chi_M T)$, its significant reduction from the room-temperature value of $(\chi_M T) = 1.1 \text{ emuK/mol}$ towards lowest temperatures was observed below 50 K, as shown in Fig.3. The electronic ground state of $(4f^n)$ ions was determined by electron-electron interaction and the spin-orbit coupling, which removed the $(2J+1)$ -fold degeneracy of each multiplet associated with a total angular momentum *J*. Resulting energy levels of the ground-state multiplet, known as Stark levels, were usually depopulated as temperature decreased from 300 K leading to the decrease of $(\chi_M T)$. Pr(III) ion $(4f^2)$ with the ground state multiplet $^3\text{H}_4$ is thus a non-Kramers ion with *g*-factor $g_J = 4/5$. The observed room-temperature experimental value of $\chi_M T$ is lower than the theoretical prediction of 1.6 emuK/mol. This could be result of several effects: not all Stark levels are populated; the exchange interaction between the Pr(III) ions is present; or a partial change of the valence from Pr(III) to Pr(IV) with $(4f^1)$ electronic configuration similar to Ce(III) ion, which is a Kramers ion. In addition, there is a possibility of the creation of the radical carrying a spin on porphyrin ligand and its exchange interaction with neighboring Pr ion. Since the exchange interaction between the $(4f)$ ions is typically very low, as shown for some dimeric $4f$ -ion-based complexes with very short exchange path through oxygen atom [9], its influence at high temperatures should be negligible.

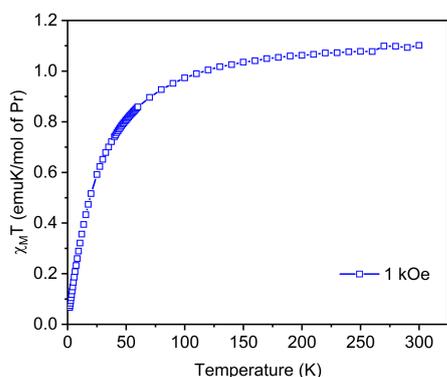


Fig. 3. Temperature dependence of $(\chi_M T)$ versus T of $\{\text{Pr}_4(\text{H}_2\text{TPPS})_3\} \cdot n\text{H}_2\text{O}\}_n$.

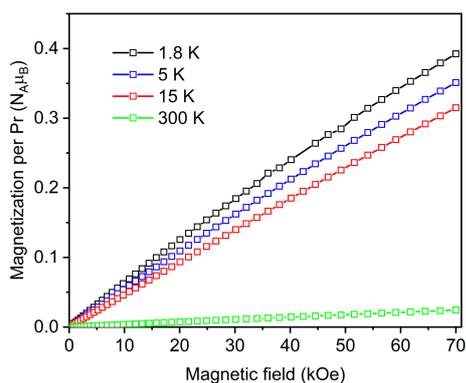


Fig. 4. Magnetization (M) versus field (H) of $\{\text{Pr}_4(\text{H}_2\text{TPPS})_3\} \cdot n\text{H}_2\text{O}\}_n$ at applied fields of 0–70 kOe at representative temperatures.

For D_{4d} symmetry of the local Pr(III) environment in studied MOF, similar to that observed in well-known $\text{Ln}(\text{Pc})_2^-$ based molecular magnets, the crystal-field parameters B_2^0 , B_4^0 , and B_6^0 in Stevens notation are necessary for the proper description of magnetic properties [10]. The ground state of non-Kramers Pr(III) in the presence of low-symmetry components of the crystal field is expected to be a non-degenerate singlet, or a quasi-doublet of two close-lying levels. Such a scenario was suggested also for Pr(III) ions in $\text{CsPr}(\text{MoO}_4)_2$ [11] with energy separation of 14 cm^{-1} within the ground quasi-doublet. A similar energy-level separation with ground-state level $M_J = 0$ would explain a small value of the magnetization reached at 70 kOe and 1.8 K (see Fig. 4), which is far from theoretical saturation of $3.2 N_A \mu_B$, and also a significant reduction of the value of $(\chi_M T)$ below 50 K to only 0.07 emuK/mol at 1.8 K. To confirm the ground state configuration and the possibility of the partial valence change of Pr ions in studied $\{\text{Pr}_4(\text{H}_2\text{TPPS})_3\} \cdot n\text{H}_2\text{O}\}_n$, further electron-paramagnetic study will be realized. However, our studies suggest, that the combination of the unique porous structure of MOF with a combination of porphyrin architecture and praseodymium ions provides perspective material for future fuel cell applications [12].

4. Conclusions

In summary, we demonstrated the successful synthesis of a new Metal-Organic Framework, containing praseodymium ions and H_2TPPS ligand. The title complex, $\{\text{Pr}_4(\text{H}_2\text{TPPS})_3\} \cdot n\text{H}_2\text{O}\}_n$, was analyzed by the various method as single-crystal X-ray diffraction, FT-IR, TG, and magnetic measurements. During magnetic measurement, we observed a significant reduction of the magnetic moment at low temperatures, which can be caused by the low symmetry of the local crystal field at the Pr ion site. A detailed study to elucidate the influence of porphyrin ligands with possible creation of radicals on the magnetic state of Pr ions will be performed in the future.

Acknowledgments

This work was supported by the VEGA project of the Ministry of Education of the Slovak Republic (No.1/0745/17) and Slovak Research and Development Agency under the contract APVV-18-0197 and APVV-15-0520.

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