

Rare-earth diphenylphosphinates as potential metal-organic frameworks

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Abstract

The possibility of rare-earth diphenylphosphinates to form metal-organic frameworks is evaluated.

Introduction

According to the new IUPAC recommendation¹, metal-organic frameworks (MOFs) are coordination compounds that have potential voids with capacity to form coordination networks, expanding themselves infinitely up to three dimensions. Hierarchically, MOFs belong to the subclass of the coordination networks, which belong to a bigger group, a much more general one denominated coordination polymers (CP). Rare-earth diphenylphosphinate (RE(dpp)₃) can be prepared by a wet process precipitation, where a lanthanide salt solution is put together with diphenylphosphinic acid solution (Hdpp). The coordination compounds formed are hardly solubilized by typically applied solvents in synthesis, being them a polar or non-polar character. Recent studies^{2,3} have shown that RE(dpp)₃ display a structure with crystalline and non-crystalline domains, they have at least two distinct crystallographic sites for the rare-earth metal and because of these characteristics these compounds are capable of originating CP. In this study, we aim to verify the capacity of RE(dpp)₃ forming metal-organic frameworks.

Results and Discussion

Coordination compounds were synthesized along with diphenylphosphinate and trivalent cations of rare-earth metals lanthanum, europium, gadolinium and lutetium. Through FT-IR analyses can be (i) confirmed the phosphinate group coordination to the RE³⁺ ion, verifying symmetrical and non-symmetrical stretches of phosphoryl bands shifts in relation to the $\nu(\text{P=O})$ e $\nu(\text{P-OH})$ stretches of the ligand and (ii) assigned the metal-ligand coordination mode, linking the $\nu(\text{POO}^-)_{\text{asymmetrical}}$ and $\nu(\text{POO}^-)_{\text{symmetrical}}$ diphenylphosphinates stretches with these vibrational modes present on Na(dpp) and NH₄(dpp) ionic compounds. This methodology is similar to the one applied on the attribution of the coordination modes of carboxylates in metallic cations⁴. Two distinct situations are observed: one where $\Delta_{\nu}(\text{POO}^-)_{\text{complex}} \sim \Delta_{\nu}(\text{POO}^-)_{\text{salt}}$, referring to a ligand-metal coordination in bridge form, and another where $\Delta_{\nu}(\text{POO}^-)_{\text{complex}} \ll \Delta_{\nu}(\text{POO}^-)_{\text{salt}}$ suggest that the coordination mode is in form of chelate. The initial RE(dpp)₃ thermal decomposition temperature,

verified by TG/DTA analysis, is almost twice as big as the Hdpp (Hdpp ~250 °C; RE(dpp)₃ ~475 °C). This thermal behavior is comparable to inorganic phosphates. Besides, a very subtle glass transition can be noticed on the thermograms. The complex specific superficial areas were obtained by BET curves through N_{2(g)} adsorption, being found the values 55, 107, 88 e 64 m².g⁻¹, respectively, for RE(dpp)₃ with TR³⁺ = La³⁺, Eu³⁺, Gd³⁺ e Lu³⁺. The pores medium diameters vary from 47 Å to 77 Å. The Eu³⁺ coordination compounds were submitted to UV excitation Luminescence Spectroscopy (77 K). With this analysis, it was possible to observe the existence of a chemical environment surrounding that ion, with different crystallographic centers: one of high symmetry and another with D_{3h} point group or inferior. It was also possible to calculate the Judd-Ofelt parameters: $\Omega_2 = 2,87; 1,97; 3,45 \cdot 10^{-20} \text{ cm}^2$ and $\Omega_4 = 2,85; 3,40; 1,54 \cdot 10^{-20} \text{ cm}^2$, for the excitations centered in 270, 391,5 e 463,4 nm, respectively. This data are in agreement to past studies³. Through these values, it was possible to check that the ligand-metal bond O-Eu has strongly ionic characteristics.

Conclusion

RE(dpp)₃ present themselves practically insoluble in several polar or non-polar solvents. The low complexes specific superficial area can be the result of the presence of the own synthetic route remain residues, physically adsorbed in the material pores interior (e.g ligand and/or metal excess and solvent). However, the existence of large pores on the compounds structure (with diameters up to 7,7 nm), besides the presence of two distinct rare-earth symmetry center on the synthesized coordination compounds and combined to the fact of RE(dpp)₃ presents high thermal stability (superior to the thermal decomposition temperature of the precursor acid) indicate that the coordination polymers originate metal-organic frameworks.

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