Poster

Structural, conductive and precursor properties of heterometallic compounds containing alkylammonium cations

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An intriguing new application of coordination compounds as proton-conducting materials in electrochemical devices, as key components for the safety and efficiency of fuel cells, has been found due to their great porosity, crystallinity, designability and adjustability of structure and properties. In addition, the development of proton conductors that respond to stimuli is of interest not only in terms of practical applications such as drug delivery, sensors, memory and display devices, but also to gain a better understanding of proton transport pathways. The incorporation of a counterion such as hydronium (H_3O^+) or ammonium [NH_4^+, $(CH_3)_2NH_2^+$,...] during synthesis to produce charged compounds is the simplest way to introduce proton carriers. Proton-conducting pathways are created when the counterions form hydrogen-bonding arrays with the guest water or other chemical constituents. So humidity as a conducting medium is thus closely related to the excellent proton conductivity of some metal-organic compounds, which have proven to be interesting systems for modelling hydrogen-bonding networks due to the wide range of possible configurations. Although two-dimensional (2D) and three-dimensional (3D) assemblies often exhibit high proton conductivity, low- dimensional structures can also show excellent proton conductivity properties via the hydrogen-bonding chain, as a small void space can be advantageous for proton hopping [1].

The use of heterometallic complexes as single-source precursors provides alternative synthetic routes to access mixed metal oxides at moderate temperatures, obtained after reconstruction of the molecular bonding topology and removal of supporting organic groups. The advantage of a solid phase transition is the retention of the elemental composition defined by the molecular precursor, with only a loss of volatile decomposition products A higher organic content in the starting materials allows for greater porosity and smaller particle sizes in the decomposition products, which is due to greater gas release during thermolysis [2]. To date, there is no photocatalytic oxide material that meets all the practical requirements for successful use in solar water splitting and environmental remediation (e.g., dye degradation), such as high durability, optimal narrow band gap for full utilization of the entire solar spectrum, long lifetime of the photogenerated electron-hole pairs, low cost, environmental friendliness, high efficiency and stability. In this sense, it is extremely important to develop a rational design by optimizing the existing synthesis strategies, which may consequently lead to well-organized and visible light-driven photocatalysts with long lifetime.

Structural and conductive properties of novel heterometallic [$Mn^{II}Cr^{III}$] and [$Co^{II}Cr^{III}$] compounds with different nuclearity and dimensionality, will be presented as part of our ongoing research program to design and characterize novel heteropolynuclear complexes with the aim of creating potentially new functional materials [1,2]. To synthesize heterometallic compounds and also incorporate alkylammonium counterions as proton carriers, we used an aqueous solution of $[A]_3[Cr(C_2O_4)_3]$ [A = $(CH_3)_2(C_2H_5)NH^+$ or $(CH_3)(C_2H_5)_2NH^+$] as a building block in reaction with manganese(II), or with cobalt(II) ions with the addition of 2,2′;6′,2″-terpyridine (terpy). Considering the thermal decomposition of the metal-organic complexes used in the fabrication of the oxide materials, the investigated compounds were effectively utilized for the preparation of spinel oxides in one step without repeating grinding procedures and high annealing temperatures, indicating their great potential as photocatalysts for the removal of organic compounds from wastewater under visible irradiation.

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[2] Lozančić, A., Burazer, S., Šenjug, P., Renka S., Molčanov, K., Pajić, D., Androš Dubraja, L. & Jurić, M. (2024). *J. Alloys Compd.* **986**, 174087.

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