

^{129}Xe NMR Spectroscopy Study of Porous Cyanometallates

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Zinc and cadmium hexacyanocobaltates(III) were prepared, and their porous networks were explored using ^{129}Xe spectroscopy. The crystal structures of these two compounds are representative of porous hexacyanometallates, cubic ($Fm-3m$) for cadmium and rhombohedral ($R-3c$) for zinc. In the cubic structure, the porosity is related to systematic vacancies created from the elemental building block (i.e., the hexacyanometallate anion), whereas the rhombohedral ($R-3c$) structure is free of vacant sites but has tetrahedral coordination for the zinc atom, which leads to relatively large ellipsoidal pores communicated by elliptical windows. According to the Xe adsorption isotherms, these porous frameworks were found to be accessible to the Xe atom. The structure of the higher electric field gradient at the pore surface ($Fm-3m$) appears and is accompanied by a stronger guest–host interaction for the Xe atoms and a higher capacity for Xe sorption. For cadmium, the ^{129}Xe NMR signal is typical of isotropic movement for the Xe atom, indicating that it remains trapped within a spherical cavity. From spectra recorded for different amounts of adsorbed Xe, the cavity diameter was estimated. For the zinc complex, ^{129}Xe NMR spectra are asymmetric because of the Xe atom movement within an elongated cavity. The line-shape asymmetry changes when the Xe loading within the porous framework increases, which was ascribed to Xe–Xe interactions through the cavity windows. The Xe adsorption revealed additional structural information for the studied materials.

1. Introduction

Cyanometallates form a family of porous molecular materials with relatively large amounts of free space (pore volume) and small access windows. Such structural features are attractive for the separation and storage of small molecules. In this sense, porous hexacyanocobaltates have been used, for instance, in the study of molecular hydrogen storage in molecular porous materials.^{1–3} Some nitroprussides (pentacyanonitrosylferrates), for instance, are the most efficient H_2 storage materials on the basis of porous coordination compounds reported to date.⁴ However, the porous framework properties of cyanometallates remain poorly documented, even when these compounds show a high flexibility to modulate the geometry, size, and physical features of the pore system. This communication represents a contribution in that sense. The porous nature of the cyanometallate structure is related to the coordination adopted by the metal (M) that forms the salt of the involved complex cyanometallate anion. In hexacyanometallates(III) of divalent transition metals, for instance, two types of porous frameworks are found. When the metal adopts an octahedral coordination, one-third of the anionic octahedral block sites remain vacant to form a network of large pores (ca. 8.5 Å) communicated by relatively small windows (ca. 4.2 Å) (interstitial free spaces).⁵ However, when the metal is tetrahedrally coordinated to the N ends of the CN groups, a porous framework is also obtained but without vacant sites in

the crystal structure.⁶ In this case, the resulting pores have an ellipsoidal form (ca. $5.1 \times 12.7 \times 8.3$ Å) and are communicated by elliptical windows (ca. 3.9×5.2 Å⁷). Cadmium and zinc hexacyanocobaltates(III) (cubic, $Fm-3m$) and rhombohedral ($R-3c$, based on a hexagonal cell) crystal structures, respectively, are representative of these two porous frameworks and also of porous hexacyanometallates (Prussian blue analogues). Anhydrous samples of these two compounds were studied from Xe adsorption isotherms and ^{129}Xe NMR spectra, and the obtained results are discussed in this contribution. Mixed Zn–K hexacyanoferrate(II) and its analogues of Na, Rb, NH_4 , and Cs also crystallize in the $R-3c$ rhombohedral cell,⁸ but their pores were found to be inaccessible to Xe, even under pressure and at high temperature. Such behavior was attributed to the exchangeable cations that are situated close to the pore windows. Cadmium and zinc nitroprussides were initially included in this study, but their porous frameworks were also found to be inaccessible to the Xe atom. To the best of our knowledge, this is the first study using ^{129}Xe NMR spectroscopy on this family of porous materials.

2. Experimental Section

The studied samples were prepared using the precipitation method. Hot aqueous solutions (0.01 M at ~ 90 °C) of zinc and cadmium sulfates and of $\text{K}_3[\text{Co}(\text{CN})_6]$ were mixed under stirring, and the precipitate that was formed was aged 2 days within the mother liquor. The obtained solids were separated by centrifugation, washed several times with distilled water, and then air-dried at 60 °C. All the reagents used were analytical grade and were obtained from Sigma-Aldrich. The nature of the obtained powders as hexacyanometallates was verified from infrared (IR) spectra, and their stoichiometry was inferred from the atomic ratio of the involved metals, which was estimated from X-ray fluorescence analyses. The

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