Structural Insights into Metal-Organic Connectivity by Paramagnetic NMR

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Abstract

Metal-Organic Frameworks (MOFs) are an emerging class of materials with numerous applications in domains such as gas storage and separation, catalysis and bioimaging [1]. They consist of metallic centres with organic linkers between them, forming a 3D network. These MOFs are difficult to analyze through x-ray diffraction (XRD) methods, thus the hope is that Nuclear Magnetic Resonance (NMR) will provide meaningful insight into their structures. However, many MOFs are paramagnetic, as many positive ions of transition metals contain unpaired electrons. Paramagnetic electrons introduce complications to NMR studies of such compounds. Along with these complications, opportunities to probe chemical structure through paramagnetic interactions arise.
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Introduction

Metal-Organic Frameworks (MOFs) are an emerging class of materials with numerous applications in domains such as gas storage and separation, catalysis and bioimaging [1]. They consist of metallic centres with organic linkers between them, forming a 3D network. These MOFs are difficult to analyze through x-ray diffraction (XRD) methods, thus the hope is that Nuclear Magnetic Resonance (NMR) will provide meaningful insight into their structures.

However, many MOFs are paramagnetic, and as many positive ions of transition metals contain unpaired electrons. Paramagnetic effects introduce complications to NMR studies of such compounds. Along with these complications, opportunities to probe nuclear relaxation through paramagnetic interactions arise.

Purpose

The goal of this project is to make use of the sensitivity of NMR to unpaired electrons to gain insight into the packing structures of ligands in these materials, with the hope that paramagnetic NMR may be extended to a wider variety of MOFs.

Theory of Paramagnetic NMR

Most NMR is performed on diamagnetic compounds. The magnetic moment of paramagnetic electrons results in significant interactions with the nuclei in a material. These interactions drastically alter the NMR spectrum by two mechanisms.

Isotropic Hyperfine (Fermi):

A through-bond effect, which originates in unpaired-electron spin-density (\(\rho\)) having a probability to exist at a given nucleus. This interaction results in changes to the observed NMR shifts (\(\delta_{\text{obs}}\)) according to:

\[
\delta_{\text{obs}} = \delta_{\text{dia}} + \delta_{\text{sp}} + \delta_{\text{F}}
\]

where \(\delta_{\text{dia}}\) is the diamagnetic shift, \(\delta_{\text{sp}}\) is the total electron spin number, \(T\) is the temperature of the system, and \(M\) has a value of 2.35 x 10^10 ppm K^-1.

Anisotropic Hyperfine (Dipolar):

The dipolar effect is a through-space interaction between nuclei and unpaired electrons with effects that include dramatic increases in nuclear relaxation rates.

The nuclear relaxation time, \(T_1\), is a significant factor in terms of experimental NMR. Relaxation times vary drastically with interatomic distance r, as \(T_1 \propto r^{-6}\). A shorter relaxation period indicates a closer proximity to paramagnetic metal centres, r, the source of unpaired electrons. Nuclear \(T_1\) is measured experimentally and compared with theory to gain structural insight.

\[
T_1 = \frac{25S(S+1)J^2g_I^2g_e^2}{15\hbar^2}
\]

Methods

• Apparatus Used:
  - Bruker Avance III 500 Spectrometer
  - 12 mm Magic Angle Spinning (MAS) Probe
  - 60-60 kHz MAS Rate

• Experiments Performed:
  - 31P, 13C, 1H Hahn-Echo
  - 13C/1H REDOR used to distinguish carbons bonded to hydrogen from those not bonded to hydrogen.
  - Saturation Recovery and Inversion Recovery to measure \(T_1\)
  - CP/MAS to measure \(T_1\) where a 2 pulse is followed by a train of x pulses to measure the rate of longitudinal coherence decay, for which \(T_2\) is the time constant.

• Synthesis:
  - Samples were synthesized by Daniel Padeanu and Dr. George Shimizu.

Structures

These samples consist of octahedral chromium nodes connected to phosphonate groups via water hydrogen bonds. The 3D framework is formed through phosphinate based organic linkers. see figure 2. Unpaired electrons from the d^6 Cr^3+ centres, are delocalized throughout the framework structure, and confer paramagnetic character on the nuclei of interest.

Discussion

• The effects of the Fermi coupling shift the peaks to higher frequency, demonstrating the similar spin delocalization pathways and hence structural connectivity of these samples.

Conclusions

• The sensitivity of NMR peak shifts to paramagnetic electrons has been used to begin developing an understanding of metal-organic connectivity in MOFs.

• By comparison to other structures, insight has been gained on the packing arrangement of the biphenyl structure.

• A more quantitative model for interpreting paramagnetic relaxation rates within these, and other periodic systems could potentially triangulate atomic positions.

• This sort of analysis can be extended to similar structures, such as other MOFs, to assist in the development of frameworks with specific and useful properties.

References


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