

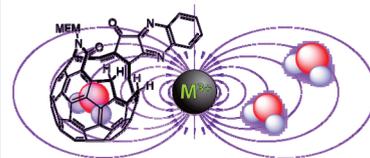
# Magnetic Interaction of Solution-State Paramagnets with Encapsulated H<sub>2</sub>O and H<sub>2</sub>

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**ABSTRACT** The bimolecular contribution,  $R_1$  ( $M^{-1} s^{-1}$ ), to the  $T_1$  of isolated H<sub>2</sub> and H<sub>2</sub>O protons, as well as free H<sub>2</sub>O in organic solution, by paramagnetic metal complexes was determined. Isolation was achieved by encapsulation in a fullerene: H<sub>2</sub> was trapped in pristine C<sub>60</sub> or in C<sub>60</sub> with a 13-atom opening, and H<sub>2</sub>O in an open-C<sub>60</sub> with a 19-atom opening. The  $R_1$  values in the presence of the various M(acac)<sub>x</sub> complexes [M = Fe(III), Cr(III), Cu(II), Co(III)] scale with  $\mu_{\text{eff}}^2$  of the metal complex. The  $R_1$  values were significantly smaller for the trapped species than the free H<sub>2</sub>O. Surprisingly,  $R_1$  was nearly identical for the all three endohedral proton pairs, even in different solvents. This suggests that the magnetic isolation effects of the carbon cage are not significantly affected by the solvent, the completeness of the carbon cage, or separation of the hydrogens by an oxygen atom.

**SECTION** Kinetics, Spectroscopy



The subject of water in hydrophobic environments is of increasing interest,<sup>1</sup> especially as improving elucidation of protein structure raises questions about the presence of single (or several) H<sub>2</sub>O molecules in hydrophobic pockets created by peptide folding.<sup>2</sup> The host/guest nature of smaller, well-defined supramolecular systems provides an opportunity for exploration of confined H<sub>2</sub>O/hydrophobic interactions, as well as many additional applications. Recently, H<sub>2</sub>O and many other guest atoms and small molecules have been inserted into the hydrophobic carbon “cage” host of C<sub>60</sub> and its derivatives.<sup>3,4</sup> It has been subsequently found that the host can affect the internal motion of the guest,<sup>5</sup> and the guest can affect the reactivity of the cage.<sup>6</sup> NMR has proven an excellent tool for probing host/guest spin interactions in well-defined hosts such as clathrates.<sup>7</sup> For C<sub>60</sub> as a host, resonances from encapsulated NMR-active nuclei (<sup>3</sup>He, <sup>1</sup>H) are shifted upfield away from other signals by the shielding effects of the ring currents of the C<sub>60</sub> cage. This is known as the *endohedral effect*. Other magnetic effects are seen in the endohedral fullerene H<sub>2</sub>@C<sub>60</sub>, where the confined motion of the H<sub>2</sub> dramatically changes its spin–lattice relaxation rate, and the carbon cage changes the bimolecular contribution (relaxivity)  $R_1$  ( $M^{-1} s^{-1}$ ) to the  $T_1$  by paramagnetic species in the solvent.<sup>8</sup> In addition, the fullerene slows the rate of the ortho/para conversion of the H<sub>2</sub> so that enriched *p*H<sub>2</sub> inside C<sub>60</sub> is stable for weeks.<sup>9</sup>

Openings in the C<sub>60</sub> cage large enough to accommodate H<sub>2</sub>O can be produced through a series of scissions that result in permanent 18-, 19-, or 20-atom orifices.<sup>3,4,10</sup> Surprisingly, it was found that the C<sub>60</sub> with the larger openings spontaneously

and reversibly encapsulate a H<sub>2</sub>O molecule from the trace water in organic solvents at ambient temperatures. Other open fullerenes (e.g., structure **3**; see Chart 1) encapsulate H<sub>2</sub>O at temperatures above room temperature. H<sub>2</sub>@C<sub>60</sub> (**1**) is synthesized via a series of cage scissions resulting in a 13-atom opening into which H<sub>2</sub> can be inserted (structure **2**) at 800 atm at 200 °C (this opening is subsequently closed to produce **1**). Once H<sub>2</sub> or H<sub>2</sub>O is inserted, the host/guest compounds **1–3** are stable at room temperature.<sup>3,11,12</sup>

These trapped water and hydrogen endofullerene systems can be thought of as a family of confined pairs of coupled molecular fermions (coupled protons). According to the Pauli principle, they exist as two nuclear spin isomers (*o*H<sub>2</sub>/*p*H<sub>2</sub> and *o*H<sub>2</sub>O/*p*H<sub>2</sub>O). External perturbations affecting the magnetic environment inside the cage can be probed by measuring the interactions of the protons with a strong external paramagnet, for instance in the interconversion of the *o*H<sub>2</sub>/*p*H<sub>2</sub> pair. Metal ions coordinated by acetylacetonate groups with the generic formula M(acac)<sub>x</sub>, M = Cu(II), Cr(III), and Fe(III), provide a series of highly paramagnetic species with one, three, and five unpaired electrons, respectively. Additionally, Co(acac)<sub>3</sub> is a structurally similar but diamagnetic control. Aside from magnetic effects, these complexes should have little specific interaction with the C<sub>60</sub> cage, and they are soluble in organic solvents.

**Received Date:** March 15, 2010

**Accepted Date:** April 9, 2010

**Published on Web Date:** April 15, 2010

Chart 1. Structures of 1, 2, and 3

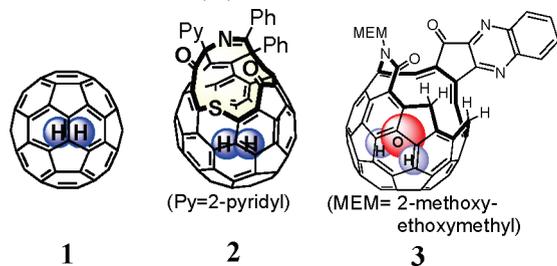


Table 1. Relaxivities of Free H<sub>2</sub>O, Encapsulated H<sub>2</sub>O and H<sub>2</sub>, and the Magnetic Moment of Each M(acac)<sub>x</sub>

M	$\mu_{\text{eff}}$ (bohr magnetons)	$R_1 = \text{relaxivities (M}^{-1} \text{ s}^{-1}\text{)}$			
		H <sub>2</sub> O <sup>a</sup>	3 <sup>a</sup>	2	1 <sup>b</sup>
Co	0	0	0	0 <sup>b</sup>	0
Cu	0.99 <sup>13</sup>	1000	80	70 <sup>a,c</sup>	— <sup>d</sup>
Cr	3.86 <sup>14</sup>	2300	220	225 <sup>b</sup>	235
Fe	5.93 <sup>15</sup>	4500	520	475 <sup>b</sup>	525

<sup>a</sup> In chloroform-d<sub>1</sub>. <sup>b</sup> In 1,2-dichlorobenzene-d<sub>4</sub>. <sup>c</sup> Sparingly soluble in CDCl<sub>3</sub>. <sup>d</sup> Not soluble together.

Measuring the relaxivity,  $R_1$ , of the endohedral H<sub>2</sub>O protons in **3**, as well as those of H<sub>2</sub> in **1** and **2** with the metal ions should provide a unique basis for comparison of and insight into the magnetic isolation effects created by these cages. Understanding the magnetic relaxation properties of this unique host/guest system has additional applications for nuclear polarization and hydrogen storage, as well as perhaps even as a practical means for the creation and application of enriched pD<sub>2</sub>O.

The relaxivity,  $R_1$ , of water or H<sub>2</sub> protons by a paramagnetic complex,  $P$ , is defined via eq 1:

$$1/T_1 = 1/T_1^0 + R_1[P] \quad (1)$$

where  $T_1^0$  is the relaxation time in the absence of  $P$ , and  $[P]$  is in units of molarity. The values of  $R_1$  obtained in this way are presented in Table 1. It is apparent that (1)  $R_1$  increases with the magnitude of the magnetic moment of the paramagnet,  $\mu_{\text{eff}}$ , (2) there is a remarkable similarity of the magnitudes of  $R_1$  for water protons in the open fullerene and H<sub>2</sub> in open and closed fullerenes, and (3)  $R_1$  of free water for the same  $P$  is an order of magnitude larger than that for the caged species.

It seems likely that, in the present case, spin–lattice relaxation should occur by an outer-sphere mechanism, arising from the dipole–dipole interaction between the spins. If it is further assumed that both the proton carriers and the acac complexes behave as classically diffusing spheres of about the same size,  $R_1$  (M<sup>-1</sup> s<sup>-1</sup>) at high magnetic fields is expected to follow<sup>16</sup>

$$R_1 = 8000\pi^2\gamma_H^2\eta\mu_B^2\mu_{\text{eff}}^2(\mu_0/4\pi)^2N_A/25k_B T \quad (2)$$

where  $\gamma_H$  is the proton magnetogyric ratio,  $\eta$  the viscosity of the medium,  $\mu_{\text{eff}}$  is the effective magnetic moment of  $P$  in units of the bohr magneton,  $\mu_B$ ,  $N_A$  is the Avogadro constant, and all units are SI. From eq 2  $R_1$  is predicted to scale as  $\mu_{\text{eff}}^2$  at a given  $T$ .

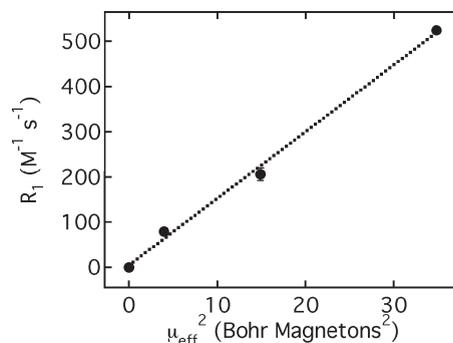


Figure 1. Relaxivities of endohedral H<sub>2</sub>O protons in **3** versus the square of the magnetic.

A plot of  $R_1$  versus the value of  $\mu_{\text{eff}}^2$  is presented in Figure 1. Figure 1 shows that the  $\mu_{\text{eff}}^2$  dependence accurately describes observation 1 as a square dependence on  $\mu_{\text{eff}}$  is expected from eq 2. Furthermore, observation 2 is also predicted from eq 2, which is notably independent of the structure of the proton carrier or  $P$ , a feature of the model first employed by Bloembergen, Purcell, and Pound to estimate values of  $\mu_{\text{eff}}$  for metal ions in their classic treatment of nuclear relaxation.<sup>17</sup>

The more effective relaxation of free water, observation 3, might be attributed to a breakdown of the approximations leading to eq 2 or an inner-sphere contribution to the relaxation mechanism. The former explanation may be tested by substitution of appropriate viscosities and other parameters into eq 2. This yields a calculated value of ca. 230 M<sup>-1</sup> s<sup>-1</sup> for Cr(acac)<sub>3</sub> in CDCl<sub>3</sub>, which is remarkably close to the value observed for all three of the caged species. It seems likely, therefore, that the larger relaxivity of free water indicates additional bimolecular contributions.<sup>16,17</sup>

The similarities between the  $R_1$  values for the three sets of endohedral protons for a given M(acac)<sub>x</sub> also indicates that the relaxivity is insensitive to differences in cage shape, cage completeness, or even the presence of an oxygen atom between the protons (water). Additionally, the solubility of **3** in multiple solvents permitted  $R_1$  measurements of *endo*-H<sub>2</sub>O in 1,2-dichlorobenzene-d<sub>4</sub> and CDCl<sub>3</sub>. As indicated above, no solvent dependence of  $R_1$  was measured; however, a weak solvent dependence was observed when comparing  $T_1^0$  without M(acac)<sub>x</sub> present. The  $T_1^0$  values without relaxant, approximately 0.1 s,<sup>8</sup> 0.2 s,<sup>12</sup> and 2.5 s, for **1**, **2** and **3**, respectively, are, however, determined primarily by the details of rotation of the caged molecules and should not reflect the changes in size or shape that would greatly affect the diffusive motion responsible for eq 2. This is somewhat unexpected, as the size of the orifice and the external solvent greatly influence other host/guest characteristics such as kinetics of escape and encapsulation equilibrium of guests in these fullerenes.<sup>18,19</sup>

In conclusion, it is apparent that the relaxivities of trapped water and hydrogen in either open or closed C<sub>60</sub> in the presence of M(acac)<sub>x</sub> complexes are nearly identical. The relaxation is well described by dipole–dipole relaxation using a classical diffusion model.<sup>17</sup> These results are also of relevance to the catalysis of *para*–*ortho* conversion of H<sub>2</sub> in fullerene cages. It has already been shown for the conversion of H<sub>2</sub> in acetonitrile solution by various metal spin catalysts

that the process exhibits a  $\mu_{\text{eff}}^2$  dependence.<sup>20</sup> Extension of such studies to fullerene cages will provide an interesting comparison with the results reported here.

## EXPERIMENTAL METHODS

Compounds **1**, **2**, and **3**, were prepared using previously published techniques.<sup>3,11,12</sup> Typically, incorporation percentages were > 90% for H<sub>2</sub> in **1** and **2** and ~75% for H<sub>2</sub>O in **3**. For a typical relaxivity measurement, 1–2 mg of fullerene was dissolved in 500  $\mu\text{L}$  of either chloroform-d<sub>1</sub> (**3**) or 1,2-dichlorobenzene-d<sub>4</sub> (**1** and **2**). Increasing concentrations of M(acac)<sub>x</sub> were added via injections of a stock solution. After mixing, the T<sub>1</sub>'s of the endohedral protons were measured on a Bruker Avance 500 MHz spectrometer via the inversion recovery method. Each trapped proton pair produces a single NMR resonance for the measurement: for H<sub>2</sub>O in **3**,  $\delta_{1\text{H}} = -10.0$  ppm, for H<sub>2</sub> in **1**,  $\delta_{1\text{H}} = -1.4$  ppm, and for H<sub>2</sub> in **2**,  $\delta_{1\text{H}} = -7.2$  ppm. R<sub>1</sub> for trace free H<sub>2</sub>O in the solvent of the sample of **3** ( $\delta_{1\text{H}} = +1.6$  ppm) was also determined.

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**ACKNOWLEDGMENT** The authors thank the National Science Foundation for its continued and generous support of this research through Grant CHE 07-17518.

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