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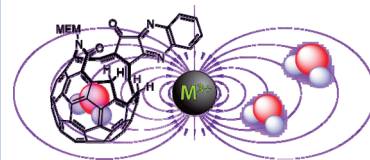
Magnetic Interaction of Solution-State Paramagnets with Encapsulated H₂O and H₂

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ABSTRACT The bimolecular contribution, R_1 ($M^{-1} s^{-1}$), to the T_1 of isolated H₂ and H₂O protons, as well as free H₂O in organic solution, by paramagnetic metal complexes was determined. Isolation was achieved by encapsulation in a fullerene: H₂ was trapped in pristine C₆₀ or in C₆₀ with a 13-atom opening, and H₂O in an open-C₆₀ with a 19-atom opening. The R_1 values in the presence of the various M(acac)_x complexes [M = Fe(III), Cr(III), Cu(II), Co(III)] scale with μ_{eff}^2 of the metal complex. The R_1 values were significantly smaller for the trapped species than the free H₂O. 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,¹ especially as improving elucidation of protein structure raises questions about the presence of single (or several) H₂O molecules in hydrophobic pockets created by peptide folding.² The host/guest nature of smaller, well-defined supramolecular systems provides an opportunity for exploration of confined H₂O/hydrophobic interactions, as well as many additional applications. Recently, H₂O and many other guest atoms and small molecules have been inserted into the hydrophobic carbon “cage” host of C₆₀ and its derivatives.^{3,4} It has been subsequently found that the host can affect the internal motion of the guest,⁵ and the guest can affect the reactivity of the cage.⁶ NMR has proven an excellent tool for probing host/guest spin interactions in well-defined hosts such as clathrates.⁷ For C₆₀ as a host, resonances from encapsulated NMR-active nuclei (³He, ¹H) are shifted upfield away from other signals by the shielding effects of the ring currents of the C₆₀ cage. This is known as the *endohedral effect*. Other magnetic effects are seen in the endohedral fullerene H₂@C₆₀, where the confined motion of the H₂ 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.⁸ In addition, the fullerene slows the rate of the ortho/para conversion of the H₂ so that enriched *p*H₂ inside C₆₀ is stable for weeks.⁹

Openings in the C₆₀ cage large enough to accommodate H₂O can be produced through a series of scissions that result in permanent 18-, 19-, or 20-atom orifices.^{3,4,10} Surprisingly, it was found that the C₆₀ with the larger openings spontaneously

and reversibly encapsulate a H₂O molecule from the trace water in organic solvents at ambient temperatures. Other open fullerenes (e.g., structure **3**; see Chart 1) encapsulate H₂O at temperatures above room temperature. H₂@C₆₀ (**1**) is synthesized via a series of cage scissions resulting in a 13-atom opening into which H₂ can be inserted (structure **2**) at 800 atm at 200 °C (this opening is subsequently closed to produce **1**). Once H₂ or H₂O is inserted, the host/guest compounds **1–3** are stable at room temperature.^{3,11,12}

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*H₂/*p*H₂ and *o*H₂O/*p*H₂O). 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*H₂/*p*H₂ pair. Metal ions coordinated by acetylacetonate groups with the generic formula M(acac)_x, 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)₃ is a structurally similar but diamagnetic control. Aside from magnetic effects, these complexes should have little specific interaction with the C₆₀ cage, and they are soluble in organic solvents.

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Chart 1. Structures of 1, 2, and 3

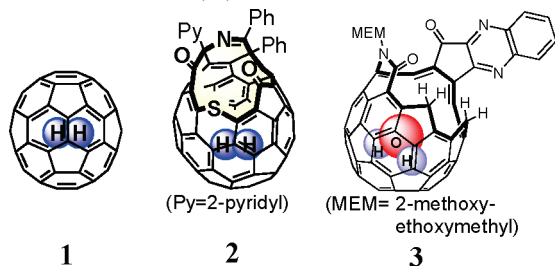


Table 1. Relaxivities of Free H₂O, Encapsulated H₂O and H₂, and the Magnetic Moment of Each M(acac)_x

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

^a In chloroform-d₁. ^b In 1,2-dichlorobenzene-d₄. ^c Sparingly soluble in CDCl₃. ^d Not soluble together.

Measuring the relaxivity, R_1 , of the endohedral H₂O protons in **3**, as well as those of H₂ 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 pH₂O.

The relaxivity, R_1 , of water or H₂ 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, μ_{eff} , (2) there is a remarkable similarity of the magnitudes of R_1 for water protons in the open fullerene and H₂ 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 ($\text{M}^{-1} \text{s}^{-1}$) at high magnetic fields is expected to follow¹⁶

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

where γ_H is the proton magnetogyric ratio, η the viscosity of the medium, μ_{eff} is the effective magnetic moment of P in units of the bohr magneton, μ_B , N_A is the Avogadro constant, and all units are SI. From eq 2 R_1 is predicted to scale as μ_{eff}^2 at a given T .

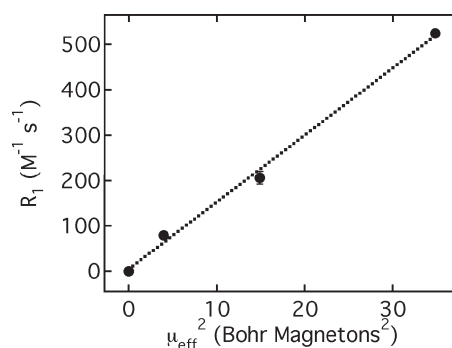


Figure 1. Relaxivities of endohedral H₂O protons in **3** versus the square of the magnetic.

A plot of R_1 versus the value of μ_{eff}^2 is presented in Figure 1. Figure 1 shows that the μ_{eff}^2 dependence accurately describes observation 1 as a square dependence on μ_{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 μ_{eff} for metal ions in their classic treatment of nuclear relaxation.¹⁷

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. $230 \text{ M}^{-1} \text{s}^{-1}$ for Cr(acac)₃ in CDCl₃, 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.^{16,17}

The similarities between the R_1 values for the three sets of endohedral protons for a given M(acac)_x 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*-H₂O in 1,2-dichlorobenzene-d₄ and CDCl₃. 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)_x present. The T_1^0 values without relaxant, approximately 0.1 s,⁸ 0.2 s,¹² 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.^{18,19}

In conclusion, it is apparent that the relaxivities of trapped water and hydrogen in either open or closed C₆₀ in the presence of M(acac)_x complexes are nearly identical. The relaxation is well described by dipole–dipole relaxation using a classical diffusion model.¹⁷ These results are also of relevance to the catalysis of *para*–*ortho* conversion of H₂ in fullerene cages. It has already been shown for the conversion of H₂ in acetonitrile solution by various metal spin catalysts

that the process exhibits a μ_{eff}^2 dependence.²⁰ 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.^{3,11,12} Typically, incorporation percentages were > 90% for H₂ in **1** and **2** and ~75% for H₂O in **3**. For a typical relaxivity measurement, 1–2 mg of fullerene was dissolved in 500 μL of either chloroform-*d*₁ (**3**) or 1,2-dichlorobenzene-*d*₄ (**1** and **2**). Increasing concentrations of M(acac)₃ were added via injections of a stock solution. After mixing, the *T*₁'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 H₂O in **3**, $\delta_{1\text{H}} = -10.0$ ppm, for H₂ in **1**, $\delta_{1\text{H}} = -1.4$ ppm, and for H₂ in **2**, $\delta_{1\text{H}} = -7.2$ ppm. *R*₁ for trace free H₂O in the solvent of the sample of **3** ($\delta_{1\text{H}} = +1.6$ ppm) was also determined.

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