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Journal of Solid State Chemistry 171 (2003) 38–43

JOURNAL OF
SOLID STATE
CHEMISTRY

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Physical characteristics of lanthanide complexes that act as magnetization transfer (MT) contrast agents

Shanrong Zhang[a] and A. Dean Sherry[a,b,*]

[a] Department of Chemistry, Berkner Science Building, University of Texas at Dallas, 2601 N. Floyd Road, P.O. Box 830688, Richardson, TX 75083-0688, USA
[b] The Rogers Magnetic Resonance Center, Department of Radiology, Southwestern Medical Center, University of Texas, 5801 Forest Park Road, Dallas, TX 75235-9085, USA

Received 4 May 2002; received in revised form 1 August 2002; accepted 11 November 2002

Abstract

Rapid water exchange is normally considered a prerequisite for efficient Gd^{3+}-based MRI contrast agents. Yet recent measures of exchange rates in some Gd^{3+} complexes have shown that water exchange can become limiting when such complexes are attached to larger macromolecular structures. A new class of lanthanide complexes that display unusually slow water exchange (bound water lifetimes (τ_M^{298}) $> 10\,\mu s$) has recently been reported. This apparent disadvantage may be taken advantage of by switching the metal ion from gadolinium(III) to a lanthanide that shifts the bound water resonance substantially away from bulk water. Given appropriate water exchange kinetics, one can then alter the intensity of the bulk water signal by selective presaturation of this highly shifted, Ln^{3+}-bound water resonance. This provides the basis of a new method to alter MR image contrast in tissue. We have synthesized a variety of DOTA-tetra(amide) ligands to evaluate as potential magnetization transfer (MT) contrast agents and found that the bound water lifetimes in these complexes are sensitive to both ligand structure (a series of Eu^{3+} complexes have τ_M^{298} values that range from 1 to 1300 μs) and the identity of the paramagnetic Ln^{3+} cation (from 3 to 800 μs for a single ligand). This demonstrates that it may be possible either to fine-tune the ligand structure or to select proper lanthanide cation to create an optimal MT agent for any clinical imaging field.

Keywords: *Ln(III) complexes*; Dota-tetra(amides); MRI contrast agents; Magnetization transfer agents

1. Introduction

Current MRI contrast agents (CAs) are largely derived from paramagnetic gadolinium complexes that shorten the relaxation time of bulk water protons in tissue by rapid exchange of at least one gadolinium-bound inner sphere water molecule with bulk solvent [1,2]. Recently, Ward et al. [3] demonstrated that image contrast may be altered by applying a frequency selective RF pulse at the resonance frequency of an NH or OH of an intrinsic amino acid, sugar, nucleotide, or other metabolite prior to collection of the imaging data. One advantage of such chemical exchange saturation transfer (CEST) agents over typical paramagnetic relaxation agents is that image contrast may be switched on-and-off at will. However, the amount of CEST agent required to produce significant water contrast may ultimately prove to be unrealistically high [4]. A later report demonstrated that a CEST effect can be detected at considerably lower molecular concentrations by using polymers that contain a large number of amide NH groups [5]. Nevertheless, as the chemical shift of diamagnetic NH or OH protons are typically within 5 ppm of bulk water, it may ultimately prove difficult to avoid off-resonance direct saturation of the bulk water signal or indirect saturation via water tightly bound to tissue macromolecules. The later effect is the basis of magnetization transfer (MT) imaging [6].

Since the first direct observation of a Eu^{3+}-bound water resonance in the ^1H NMR spectrum of $Eu(1)^{3+}$ in wet acetonitrile [7], a variety of DOTA-tetra(amide) complexes have been reported that have extremely slow bound water exchange kinetics (see structures 1–7 in

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*Corresponding author. Fax: +1-972-883-2925.
E-mail address: sherry@utdallas.edu (A.D. Sherry).

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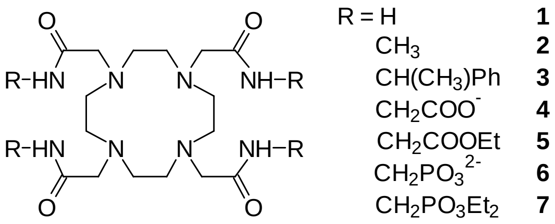
doi:10.1016/S0022-4596(02)00143-3

Scheme 1) [7–14]. The bound water lifetimes (τ_M^{298}) summarized in Table 1 show that this parameter is fine-tuned from μs to ms by slight modification of the extended pendent arms in these DOTA-like derivatives. In particular, the τ_M^{298} values of Eu(5)$^{3+}$ and Eu(7)$^{3+}$ in wet acetonitrile are ca. 789 and 1300 μs, respectively. This lifetime is long enough to observe a Eu^{3+}-bound water signal in both the ^{1}H and ^{17}O NMR spectra of Eu(5)$^{3+}$ in aqueous solution at ambient temperatures [13]. The chemical shift of the Eu^{3+}-bound water signal is ca. 50 ppm in this complex near-room temperature. This feature makes this complex very favorable compared to diamagnetic CEST agents, for avoiding off-resonance saturation of the bulk water signal in a MT-type experiment [15]. More recently, the shifted amide NH protons in paramagnetic *Ln*DOTA-tetra (amide) complexes [11,18] have also been used as an alternative and efficient MT antenna. These results have offered a new avenue for development of novel "responsive" CAs for MRI.

More recently, we have demonstrated that *Ln*$^{3+}$-bound water lifetimes are quite sensitive to the ionic radii of the central *Ln*$^{3+}$ cations in *Ln*(5)$^{3+}$ complexes in wet acetonitrile, with τ_M^{298} values ranging from several μs to ca. 800 μs for a single ligand [16]. Given that the magnitude and direction of the shifted bound water resonance in these complexes can vary over several hundred parts per million, we believe it may now be possible to design an efficient MT CA for use at any field strength either by modifying the ligand structure or by selecting the proper lanthanide cation. In this paper, we report further NMR and MRI characteristics of some *Ln*(5)$^{3+}$ complexes (where *Ln*$^{3+}$ = Pr^{3+}–Yb^{3+}, except for Gd^{3+}) as MT CAs.



Scheme 1. Structures of DOTA-tetra (amide) ligands.

2. Results and discussion

The extent of observed MT depends upon both chemical exchange and relaxation kinetics [3]:

$$\frac{M_t}{M_0} = \frac{1}{(1+k_{\rm obs}T_{\rm 1sat})} + \left[\frac{k_{\rm obs}T_{\rm 1sat}}{(1+k_{\rm obs}T_{\rm 1sat})}\right]\exp\left[-\frac{(1+k_{\rm obs}T_{\rm 1sat})}{T_{\rm 1sat}}t\right]. \qquad (1)$$

Here, M_t and M_0 are the bulk water signal intensity with and without saturation at the exchanging site, respectively; $k_{\rm obs}$ is the pseudo-first-order exchange rate between bulk water and the exchanging protons; and $T_{\rm 1sat}$ is the spin–lattice relaxation time of water protons during saturation at the exchangeable site. $k_{\rm obs}$ equals the concentration ratio of the exchanging site relative to water divided by the lifetime of the exchange site, τ_M. To observe an MT effect, the system must meet the slow exchange requirement, $\Delta\omega\tau_M \geqslant 1$. Thus, one advantage of a paramagnetic complex that displays a large $\Delta\omega$ is that faster exchange can take place (shorter τ_M) without approaching the fast exchange limit. A ^{1}H NMR signal of a *Ln*$^{3+}$-bound water can be detected in several *Ln*(5)$^{3+}$ complexes (Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Tm^{3+} and Yb^{3+}) in wet acetonitrile at temperatures ranging from −40°C to 60°C [16]. Interestingly, the chemical shift of the bound water resonance was ~2-fold larger than the chemical shift of the axial H$_4$ macrocyclic proton in those complexes where the ^{1}H NMR signal of the bound water is directly observable. This empirical relationship is useful in estimating the chemical shift of the bound water molecule in those complexes where it is

Table 1
Eu^{3+}-bound water lifetimes (τ_M^{298}) of a series of DOTA-tetra(amide) complexes (*see* structures in Scheme 1)[a]

Complexes	Isomers	τ_M^{298} (μs)	Solvent	Method	Literature
Eu(**1**)$^{3+}$	M	120	CH$_3$CN	^{1}H NMR	[7, 8]
	m	2			
Eu(**2**)$^{3+}$	**M**	156	CH$_3$CN	^{1}H and ^{17}O NMR	[9]
Eu(**3**)$^{3+}$	**M**	278	CH$_3$CN	^{1}H NMR	[10]
Eu(**4**)$^-$	**M**	40	Water, pH 8.1	^{1}H NMR	[11]
		300	Water, pH 7	^{1}H NMR	[12]
Eu(**5**)$^{3+}$	**M**	382	Water, pH 7	^{1}H and ^{17}O NMR	[13]
		789	CH$_3$CN	^{1}H NMR	
Eu(**6**)$^{5-}$	**M**	67	Water, pH 7.8	^{1}H NMR	Unpublished
Eu(**7**)$^{3+}$	**M**	1300	CH$_3$CN	^{1}H NMR	[14]

[a] It is well known that DOTA-like complexes usually coexist as two isomers in solution, the square antiprism (SAP, often called as M (means major)) and the twisted square antiprism (TSAP, m (minor)). Usually, water exchange in the M isomer is slower than in the m isomer [9,19,20].

Table 2
^{1}H chemical shifts and lifetimes (τ_M) of Ln^{3+}-bound water for $Ln(5)^{3+}$ complexes and the calculated slow exchange conditions ($\Delta\omega\tau_M$) for a variety of magnetic field strengths[a]

Complexes	^{1}H NMR observation of Ln^{3+}–H_2O	τ_M^{298} (μs)	δ (ppm)	$\Delta\omega\tau_M$		
				11.75T	4.7T	1.5T
Pr^{3+}	Yes	20	−60	3.8	1.5	0.5
Nd^{3+}	Yes	80	−32	8.0	3.2	1.0
Sm^{3+}	Yes	320	−4	4.0	1.6	0.5
Eu^{3+}	Yes	382	50	60.0	24.0	7.7
Tb^{3+}	No	31	−600	58.5	23.4	7.5
Dy^{3+}	No	17	−720	38.5	15.4	4.9
Ho^{3+}	No	19	−360	21.5	8.6	2.8
Er^{3+}	No	9	200	5.7	2.3	0.7
Tm^{3+}	Yes	3	500	4.7	1.9	0.6
Yb^{3+}	Yes	3	200	1.9	0.5	0.2

[a](1) τ_M^{298} of $Eu(5)^{3+}$ complex was directly measured for sample in aqueous solution from ^{1}H NMR linewidth fitting, and others were estimated from the corresponding lifetimes measured in wet acetonitrile, namely, τ_M^{298} (in water) $\approx \frac{1}{2}\tau_M^{298}$ (in wet acetonitrile) [16]; (2) For those complexes that the bound water was not directly observed, the chemical shift of the Ln^{3+}-bound water was estimated by doubling of the chemical shift of H_4 proton on the cyclen ring in the complexes, $\delta(Ln^{3+}\text{–}H_2O) \approx 2\delta(H_4)$ [15].

too broad to detect. A resonance characteristic of the Ln^{3+}-bound water molecule was observed or estimated (using the empirical relationship described above) at chemical shifts ranging from –720 to 500 ppm (relative to the bulk water 0 ppm) at 25°C (Table 2). The bound water lifetimes (τ_M^{298}) in these complexes were also found to vary sharply with the ionic radii of the central lanthanide cation, varying from several μs for both lighter and heavier $Ln(5)^{3+}$ complexes to 789 μs for $Eu(5)^{3+}$ [16]. For three $Ln(5)^{3+}$ complexes, water exchange was observed to be about twice as fast in neat water compared to wet acetonitrile (382 vs. 789 μs for $Eu(5)^{3+}$ [13], 159 μs [13] vs. 256 μs (unpublished)) for $Gd(5)^{3+}$, and 21 μs [17] vs. 39.2 μs (unpublished) for $Dy(5)^{3+}$). Given the assumption that τ_M^{298} (water) $\approx \frac{1}{2}\tau_M^{298}$ (acetonitrile) for the entire series of $Ln(5)^{3+}$ complexes, the τ_M^{298} values shown in Table 2 are estimated. This in turn allows estimates of $\Delta\omega\tau_M$ for the entire $Ln(5)^{3+}$ series (Table 2). This indicates that most $Ln(5)^{3+}$ complexes ($Ln^{3+} = Pr^{3+}$—Yb^{3+}) meet the slow exchange requirement at 11.75 T while only a few meet this condition at the most common clinical imaging field (only Eu^{3+}, Tb^{3+}, Dy^{3+} and Ho^{3+} meet the $\Delta\omega\tau_M > 1$ requirement at 1.5 T). This illustrates that slower exchange systems may be necessary to produce a significant MT effect at 1.5 T.

The MT efficiency of various complexes may be compared by varying the frequency of the saturation pulse and measuring the residual bulk water signal (plots of such data are referred to as Z-plots, CEST profiles or MT-profiles). Based upon the data of Table 2, we selected Pr^{3+}, Nd^{3+}, Eu^{3+} and Yb^{3+} complexes of 5 as model systems to compare the MT effects at 4.7 T. At this field, the product $\Delta\omega\tau_M$ is 24, 3.2, 1.5 and 0.5 for $Eu(5)^{3+}$, $Nd(5)^{3+}$, $Pr(5)^{3+}$ and $Yb(5)^{3+}$, respectively. MT profiles for 63 mM solutions of $Pr(5)^{3+}$, $Nd(5)^{3+}$, $Eu(5)^{3+}$ or $Yb(5)^{3+}$ are shown in Figs. 1, 2, 3 and 4, respectively. $Eu(5)^{3+}$ appears to be most favorable MT agent at 4.7 T and 25°C as a 57% decrease in bulk water intensity is observed after applying a frequency-selective RF pulse (1 s, 16.4 dB) at 50 ppm [15]. Interestingly, one

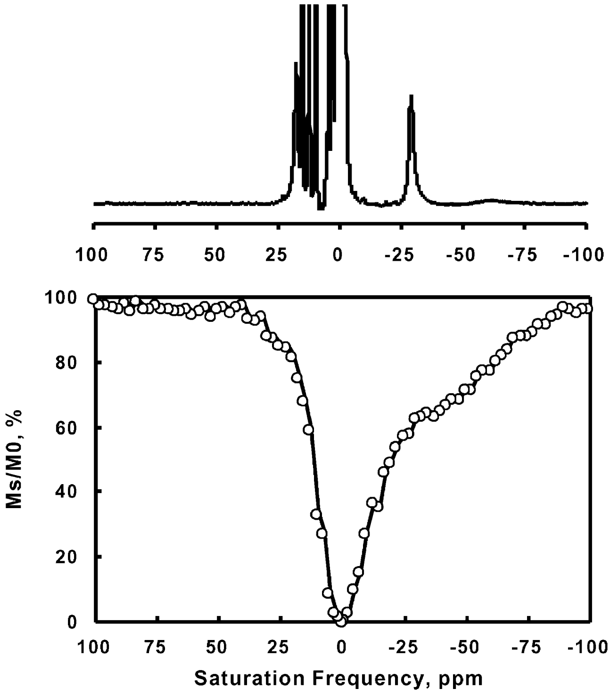


Fig. 1. Five hundred megahertz ^{1}H NMR spectrum of ~200 mM $[Pr(5)(H_2O)](triflate)_3$ acetonitrile with 2–4% H_2O and 25°C (upper; the huge bulk water peak was truncated to make the small bound water peak more visible); and an MT profile of 63 mM $[Pr(5)(H_2O)]Cl_3$ at pH 7 and ~22°C (lower). Each data point was collected by using a saturation power of 16.4 db and a duration time of 1 s on the corresponding saturation frequency. These data were obtained using a 4.7 T Brüker Omega imaging system and a ϕ 2.5 cm surface coil.

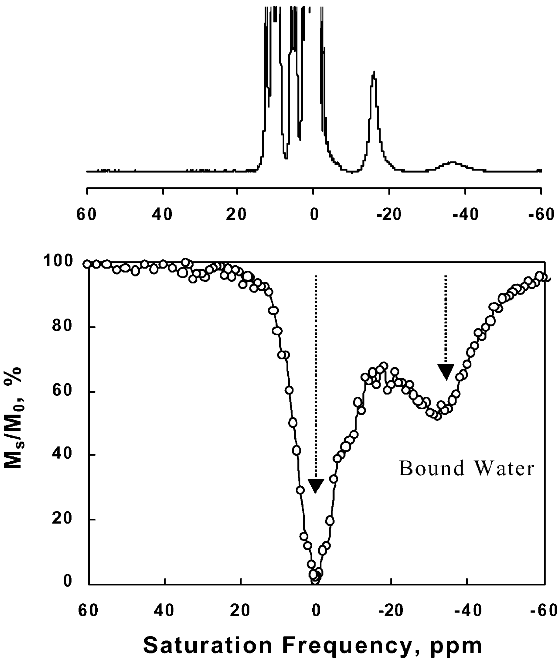


Fig. 2. Five hundred megahertz ^1H NMR spectrum of ~200 mM [Nd(5)(H_2O)](triflate)$_3$ acetonitrile with 2–4% H_2O and 25°C (upper); and an MT profile of 63 mM [Nd(5)(H_2O)]Cl_3 at pH 7 and room temperature (lower). The parameters are identical to those indicated in Fig. 1.

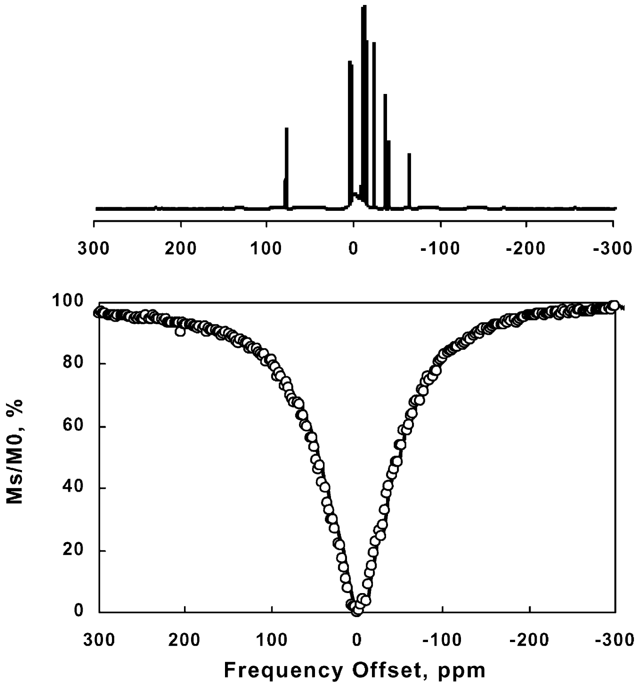


Fig. 4. Five hundred megahertz ^1H NMR spectrum of ~200 mM [Yb(5)(H_2O)](triflate)$_3$ acetonitrile with 2–4% H_2O and 25°C (upper); and an MT profile of 63 mM [Yb(5)(H_2O)]Cl_3 at pH 7 and room temperature. A saturation power of 82 dB was used. All other parameters are identical to those indicated in Fig. 1.

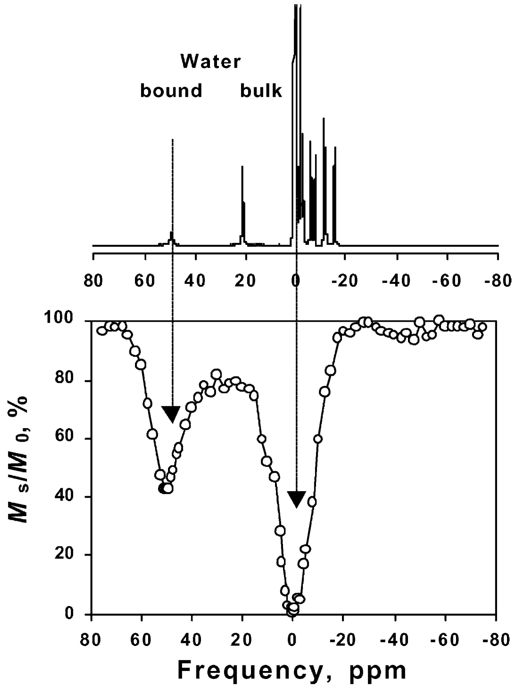


Fig. 3. Five hundred megahertz ^1H NMR spectrum of ~250 mM [Eu(5)(H_2O)]Cl_3 in aqueous solution at pH 7 and 25°C (upper); and an MT profile of 63 mM [Eu(5)(H_2O)]Cl_3 at pH 7 and room temperature. The parameters are identical to those indicated in Fig. 1.

observes a ~20% decrease in water intensity even when RF irradiation is applied at mid-frequency between the Eu^{3+}-bound and bulk water resonances (~25 ppm). This feature is expected for an unequally populated, two-site intermediate exchange system.

The MT profile of $Nd(5)^{3+}$ (Fig. 2) has features similar to those of $Eu(5)^{3+}$ except that both water resonances (metal bound and bulk) are broadened considerably. This is consistent with our previous finding [16] that water exchange is faster in $Nd(5)^{3+}$ than in $Eu(5)^{3+}$. Even so, the bulk water signal was reduced by ~48% upon saturation of the Nd-bound water resonance (1 s, 16.4 dB). This indicates that $Nd(5)^{3+}$ is ~9% less efficient than $Eu(5)^{3+}$ when both bound water resonances are saturated to the same extent. Interestingly, the bulk water signal is reduced by ~35% after applying a saturating RF pulse at a mid-frequency position between the Nd^{3+}-bound and bulk water signals (−16 ppm), ~15% greater than seen in the corresponding experiment with $Eu(5)^{3+}$. This is consistent with $Nd(5)^{3+}$ being closer to the intermediate exchange limit than $Eu(5)^{3+}$. Even faster water exchange is evident in the MT profile of $Pr(5)^{3+}$ (Fig. 1) where only a broad shoulder is detected on the low-frequency side of the bulk water resonance. In comparison to $Eu(5)^{3+}$ and $Nd(5)^{3+}$, a lower but detectable MT effect (~40%) is observed by applying an RF pulse

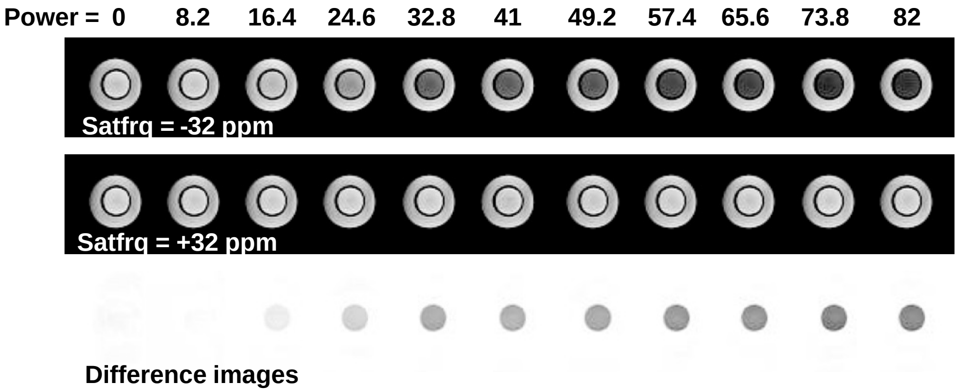


Fig. 5. MT images of a phantom containing 63 mM $Nd(5)^{3+}$ at pH 7 and room temperature. The RF irradiation power was varied (0–82 dB) at a fixed a duration time of 2 s.

(1 s, 16.4 dB) at −40 ppm. As in the prior experiments, a saturating pulse applied at an opposite frequency (in this case, +40 ppm) was used as a control. For $Yb(5)^{3+}$ (Fig. 4), no MT was evident after a saturating pulse was applied at any frequency (the Yb^{3+}-bound water resonance, detected at low temperatures in acetonitrile, is expected at 200 ppm at room temperature). Although ca. 20% of the bulk water signal can be eliminated by applying a 1 s RF pulse at ±100 ppm (Fig. 4), this is due to direct saturation of the bulk water resonance and is not an MT effect. In this case, the bulk water signal is broadened more than expected for the weakly paramagnetic Yb^{3+} ion because of intermediate-to-rapid exchange with the highly shifted bound water resonance.

Although the MT profiles demonstrate some of the important features of these exchanging systems, it is also important to demonstrate the MT effect in an actual imaging experiment. Fig. 5 illustrates images of two concentric vials, an inner vial containing 63 mM $[Nd(5)(H_2O)]Cl_3$ and a larger outer vial containing pure water. The images demonstrate that the intensity of the inner vial can be switched "on" or "off" by using frequency-selective RF irradiation of the bound water resonance. Also illustrated is the influence of saturation power on image intensity. Here, a presaturation pulse of 2 s was maintained while the saturation power was varied from 0 to 82 dB. The images show that intensity changes in the inner vial could not be detected for power levels < 30 dB and that the water intensity decrease was not altered further above 70 dB. Thus, a saturation power of 40–60 dB appears to yield the optimal MT effect without extraneous off-resonance effects. One can also hold the power constant and vary the saturation time. This is illustrated for a solution containing 63 mM $[Eu(5)(H_2O)]Cl_3$ in Fig. 6. A fit of these data of to theory (Eq. (1)) gave $T_{1sat} = 537 \pm 23$ ms and a Eu^{3+}-bound water lifetime (τ_M^{295}) of 351 ± 12 μs. Note that the T_{1sat} and τ_M values obtained from such curve fittings are usually shorter than the actual values because the bound water cannot be completely saturated due to partial relaxation. Experimentally, we found that the measured T_{1sat} and τ_M values depend upon the saturation power.

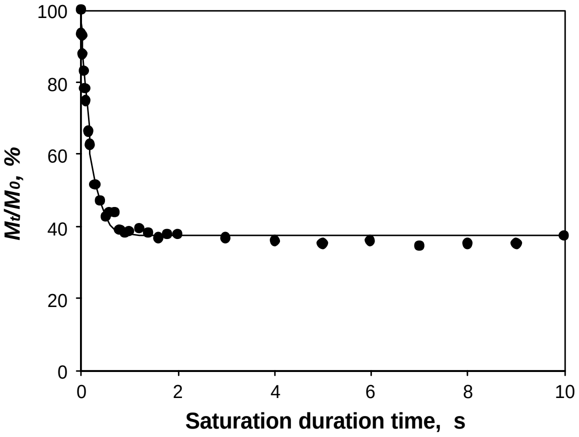


Fig. 6. M_t/M_0 dependence upon the saturation duration time for 63 mM $Eu(5)^{3+}$ at pH 7 and room temperature. An RF irradiation with a power of 16.4 dB was applied at the Eu^{3+}-bound water position (49 ppm). The solid line represents the best fit to Eq. (1) with a bound water lifetime (τ_M^{295}) of 351 ± 12 μs and a bulk water relaxation time (T_{1sat}) of 537 ± 23 ms.

3. Conclusions

We have demonstrated that paramagnetic lanthanide complexes of the DOTA-tetra(amide) ligand 5 act as efficient MT CAs [15]. Based upon the predicted chemical shift of each metal-ion-bound water molecule and available water exchange data, one can easily predict that nearly all $Ln(5)^{3+}$ complexes should work as MT agents at high magnetic field (11.75 T) while a more limited set of complexes are applicable at magnetic fields commonly used in clinical MRI scanners (1.5 T). Four complexes were more fully characterized at 4.7 T and their MT efficiencies, $Eu(5)^{3+}$ (57%), $Nd(5)^{3+}$(48%), $Pr(5)^{3+}$ (40%) and $Yb(5)^{3+}$ (∼0%), decreased as predicted the values of $\Delta\omega\tau_M$ for these complexes. This is consistent with a prior observation [18] that values of $\Delta\omega\tau_M$ near 15 are optimal for MT efficiency. These data further demonstrate that a much richer variety of lanthanide complexes might be potentially used as MT agents if their exchange sites are limited to the slow exchange condition ($\Delta\omega\tau_M \geqslant 1$). The complexes with variable bound water lifetimes provide an opportunity to select proper MT candidates at variable field strengths where the $\Delta\omega\tau_M$ value might be as close as possible to the optimal value of 15 to achieve optimal MT efficiency.

4. Experimental

Synthesis of ligand 5 and $[Ln(5)(H_2O)]X_3$ complexes had been reported previously [13], where X anions are Cl^- or triflate$^-$, respectively.

High-resolution ^1H, ^{13}C and ^{17}O NMR spectra were recorded on a Varian Inova-500 spectrometer, at observing frequency of 500, 125 and 67.7 MHz, respectively. NMR samples were allowed to stand in the probe for at least 10 min at each temperature before data acquisition. The temperature was constant to within 0.5°C.

MT profiles and ^1H T_1-weighted spin–echo images were collected using a Brüker 4.7 T Omega imaging system. The decoupler channel was used to presaturate the bound water signal. A 2.5 cm surface coil was used as receiver in all imaging experiments. Typical imaging parameters included a 1–2 s presaturation pulse with a power level of 0–82 dB (the maximum saturation power could be as high as 82 dB for this imaging system), a TE of 18 ms and a TR of 500 ms.

Acknowledgments

This work was provided in part by grants from the Robert A. Welch Foundation (AT-584), the National Institute of Health (CA-84697) and the Division of Research Resources, National Institutes of Health (RR-02584).

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