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Direct observation of Mg^{2+} complexes in ionic liquid solutions by ^{31}Mg β -NMR spectroscopy†Daniel Szunyogh,^{‡a} Ryan M. L. McFadden,^{‡b,c} Victoria L. Karner,^{‡b,c} Aris Chatzichristos,^{c,d} Thomas Day Goodacre,^e Martin H. Dehn,^{c,d} Lia Formenti,^f Derek Fujimoto,^{‡c,d} Alexander Gottberg,^e Evan Kallenberg,^d Ildikó Kálomista,^{‡a} Robert F. Kiefl,^{c,d} Flemming H. Larsen,^{‡g} Jens Lassen,^{‡e} C. D. Philip Levy,^e Ruohong Li,^e W. Andrew MacFarlane,^{b,c} Iain McKenzie,^{‡h,i} Gerald D. Morris,^h Stavroula Pallada,^a Matthew R. Pearson,^h Stephan P. A. Sauer,^{‡a} Paul Schaffer,^j Peter W. Thulstrup,^{‡a} Lars Hemmingsen*^a and Monika Stachura^{‡k}

NMR spectra of Mg^{2+} ions in ionic liquids were recorded using a highly sensitive variant of NMR spectroscopy known as β -NMR. The β -NMR spectra of MgCl_2 in EMIM-Ac and EMIM-DCA compare favourably with conventional NMR, and exhibit linewidths of ~ 3 ppm, allowing for discrimination of species with oxygen and nitrogen coordination.

Over the last few decades, β -detected nuclear magnetic resonance (β -NMR) has enjoyed use as a technique to study nuclear physics^{1,2} and condensed matter,^{3,4} the latter mainly focusing on solids, but also with applications to liquids.^{5–11} More recently, several groups have pursued advancing modern incarnations of the technique to study the solution chemistry of β -NMR probes,^{12–15} motivated by its potential to solve chemical and biochemical problems.^{16–19} With the advent of

high-intensity radioactive ion beam (RIB) facilities, many new nuclei are available in quantities sufficient for the study of condensed matter. The main challenge to the use of RIBs as probes in liquids is the incompatibility of typical solutions with high vacuum usually applied to achieve optimal RIB transport. Though specialized setups^{12,13} aim to circumvent this limitation, room temperature ionic liquids are readily compatible with high vacuum, as they exhibit virtually zero vapour pressure.²⁰ Here we demonstrate that Mg^{2+} chemical shift measurements in ionic liquids can be made with the precision necessary to discriminate between oxygen and nitrogen coordination environments using ^{31}Mg β -NMR. This resolution, required for chemical and biochemical studies, indicates that the prospect for future use in these fields is promising, and may be extended to other metal ions.

Mg^{2+} was selected as a test case because ^{31}Mg exhibits appropriate nuclear properties ($I = \frac{1}{2}$, $T_{1/2} = 236$ ms, and asymmetric β -emission^{21,22}) for β -NMR spectroscopy. Moreover, the closed shell Mg^{2+} is difficult to observe by most spectroscopic techniques, and it is an important metal ion in biological systems, involved in, e.g. ATP chemistry, nucleic acid folding, and as an integral component of chlorophyll.²³ Finally, there is considerable and rising interest in characterization of Mg^{2+} chemistry in non-aqueous solutions, such as ionic liquids, because magnesium-based batteries may outperform lithium ion batteries.²⁴ In this work, two ionic liquids were used as solvents, 1-ethyl-3-methylimidazolium acetate (EMIM-Ac), and 1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCA), aiming to probe differential chemical shifts of Mg^{2+} complexes with typical oxygen and nitrogen containing ligands, see Fig. 1. NMR spectra recorded by ^{31}Mg β -NMR and conventional ^{25}Mg NMR are presented in Fig. 2. In these experiments, anhydrous MgCl_2 was dissolved in the ionic liquids to a final concentration of 25 mM, to achieve comparable conditions in conventional NMR and β -NMR. The most important observation, and the key result of this work, is that the chemical shift differ-

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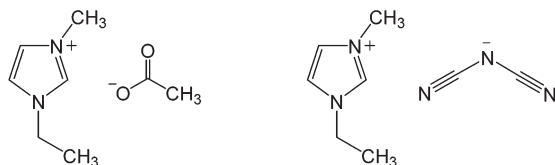


Fig. 1 Chemical structure of the two ionic liquids used as solvents in this work. Left: 1-ethyl-3-methylimidazolium acetate (EMIM-Ac); right: 1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCA).

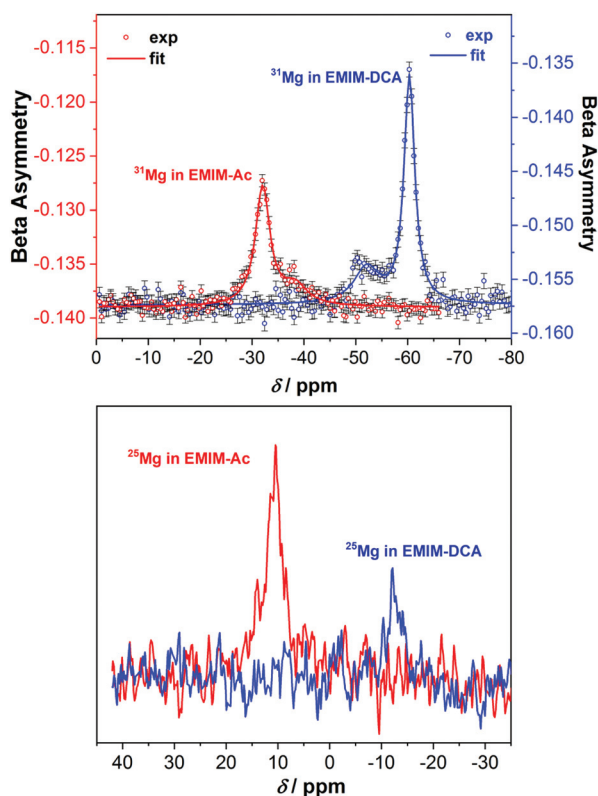


Fig. 2 ^{31}Mg β -NMR spectra (top) and conventional ^{25}Mg NMR spectra (bottom) of 25 mM MgCl_2 in EMIM-Ac (red) and EMIM-DCA (blue). The β -NMR experiments were conducted at 22 °C, ultra-high vacuum ($<10^{-9}$ mbar), and an external magnetic field of 3.41 T (45.9 MHz) using crystalline MgO as chemical shift reference. The conventional NMR experiments were conducted at 70 °C to improve signal-to-noise, ambient pressure, and an external magnetic field of 11.7 T (500 MHz) using 11 M MgCl_2 as chemical shift reference. See the text and ESI† for details.

ence for Mg^{2+} in the two ionic liquids is very similar using the two techniques. The similarity is expected if the experiments reflect the same Mg^{2+} species, and if these species exhibit rapid rotational diffusion. This establishes that ^{31}Mg β -NMR can be applied to record chemical shifts of Mg^{2+} species in solution, and that the technique provides sufficient spectral resolution to discriminate between typical coordination environments of this metal ion. *A priori*, it was not obvious that the 40 keV beam of $^{31}\text{Mg}^+$ implanted into the ionic liquids would rapidly (within the 236 ms half-life) be oxidized to Mg^{2+} , and reach the same chemical equilibrium of complexation as

observed in conventional ^{25}Mg NMR, but the spectra in Fig. 2 indicate that this is indeed the case.

Another central observation is the high resolution of the ^{31}Mg β -NMR spectrum exhibiting linewidths of ~ 3 ppm (~ 140 Hz at a resonance frequency of 45.9 MHz). This is analogous to the narrow lines observed in conventional solution (as opposed to solid state) NMR spectroscopy.²⁵ Given the small span of chemical shifts typically observed in ^{25}Mg NMR,²⁶ high resolution is essential, to discriminate different Mg^{2+} complexes. For additional discussion of the origin of the linewidth of the β -NMR resonances, see the ESI.†

The ^{31}Mg β -NMR spectrum of Mg^{2+} in EMIM-DCA displays a major resonance at -60.2 ± 2.4 ppm with respect to MgO and a weaker signal at -52.0 ± 2.4 ppm, see Fig. 2. For EMIM-Ac the main resonance is observed at -31.9 ± 2.4 ppm, with a shoulder consistent with another unresolved resonance at -38.1 ± 2.4 ppm. Thus, co-existence of two Mg^{2+} complexes is observed in EMIM-DCA and possibly in EMIM-Ac. The fact that both resonances are observed indicates no or slow exchange between them, *i.e.* the lifetime of each species is longer than milliseconds. In the conventional ^{25}Mg NMR spectra speciation is not resolved. This may either be due to the poorer signal-to-noise, faster dynamics at the higher temperature (70 °C), or nuclear quadrupole interactions (NQIs) giving rise to line broadening for ^{25}Mg ($I = 5/2$), while NQIs do not contribute to the line width for ^{31}Mg ($I = 1/2$), *vide infra*.

To demonstrate the extraordinary sensitivity of ^{31}Mg β -NMR, additional experiments were conducted at ultra-trace concentrations, with only ($\sim 10^8$ cumulative) magnesium ions originating from the $^{31}\text{Mg}^+$ RIB implanted into the sample, see Fig. 3. The spectra presented in Fig. 2 and 3 differ significantly, because 25 mM non-radioactive MgCl_2 was added for the data displayed in Fig. 2, while none was added for the data displayed in Fig. 3. Thus, the speciation observed in Fig. 3 may originate from trace amounts of high affinity ligands (such as water) for Mg^{2+} , while these impurity sites are essentially saturated in Fig. 2, shifting the spectrum towards pure DCA coordi-

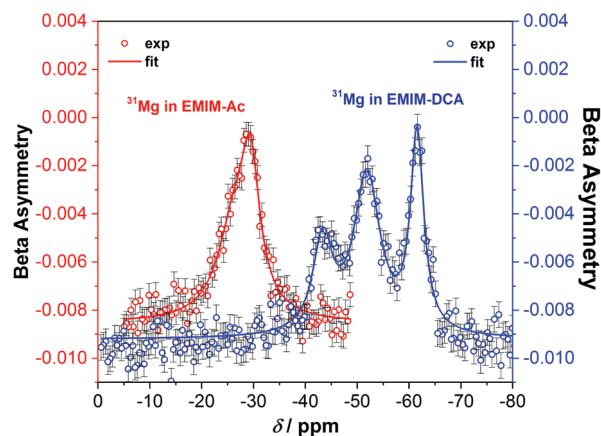


Fig. 3 ^{31}Mg β -NMR spectra recorded with ultra-trace amounts ($\sim \text{pM}$) of ^{31}Mg in EMIM-Ac (red) and EMIM-DCA (blue). The chemical shift reference is crystalline MgO . See the text for additional details.

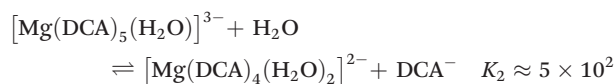
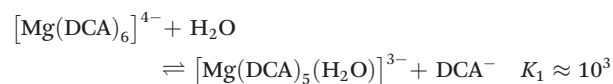


nation. Given the current and energy of the $^{31}\text{Mg}^+$ beam, the half-life (236 ms), the beam-sample geometry, and sample volume, the ^{31}Mg concentration may be estimated to be 0.1 pM–1000 pM, depending on the diffusion coefficient of Mg^{2+} in the ionic liquid. The actual concentration of Mg^{2+} is presumably higher and dictated by the trace amounts that may be present in the ionic liquids (<3.5 μM , see Table S1†). Interestingly, the two resonances observed with 25 mM Mg^{2+} in EMIM-DCA, Fig. 2, still appear to be present in the spectrum recorded with $\sim\text{pM}$ ^{31}Mg , Fig. 3, presumably reflecting the same two species. The minor species observed at -51.7 ppm however, becomes more prominent, and an additional (third) resonance is present above the noise level. The fact that the relative intensity of the two latter resonances increases when no MgCl_2 is dissolved in the ionic liquid prior to implantation of $^{31}\text{Mg}^+$ support the notion that they may originate from coordination by water or other dilute impurities with higher affinity for Mg^{2+} than DCA in the ionic liquid. Moreover, they are observed at chemical shifts closer to that of oxygen coordination (in EMIM-Ac), corroborating that they originate from water replacing DCA in the first coordination sphere. The resonance of ^{31}Mg in EMIM-Ac with ultra-trace amounts of Mg^{2+} is slightly shifted and somewhat broadened as compared to the signal observed with 25 mM MgCl_2 , Fig. 2 and 3. This may also reflect coordination by water or other impurities, and the observation that only a minor change occurs, agrees with the expectation that replacing one oxygen coordinating ligand (acetate) with another (water) leads only to small changes in chemical shift.

Complementary experiments using ^1H -, ^{13}C -, ^{15}N -, ^{25}Mg -, and ^{35}Cl -NMR spectroscopy, and FTIR spectroscopy, see Fig. S1–S9, and Tables S1–S6,† indicate that the ionic liquid anions (acetate and DCA respectively) coordinate to Mg^{2+} in rapid exchange with free anions, that the DCA anions coordinate with the terminal nitrogen, and that trace amounts of impurities such as water in the ionic liquids may give rise to the observed speciation, see Fig. 2 and 3. These observations agree with the μs residence time of water molecules reported

at 25 °C for the aqua ion of Mg^{2+} ,²⁷ with crystal structures of $\text{Mg}(\text{DCA})_2(\text{s})$ and $\text{Mg}(\text{DCA})_2(\text{H}_2\text{O})_4(\text{s})$,^{28,29} and with hard-soft-acid-base theory.^{30,31} To further substantiate the structural interpretation of the recorded ^{31}Mg β -NMR data, we present calculated NMR properties for selected Mg^{2+} complexes in Table 1.

In agreement with the ^{31}Mg β -NMR experimental data, nitrogen coordination (DCA) gives rise to shielding as compared to oxygen coordination. Accordingly, the consecutive replacement of DCA anions with water molecules gives rise to deshielding, and a tentative interpretation that accounts for the main observed β -NMR resonances for Mg^{2+} in EMIM-DCA is $[\text{Mg}(\text{DCA})_6]^{4-}$ (-60.2 ppm), $[\text{Mg}(\text{DCA})_5(\text{H}_2\text{O})]^{3-}$ (-52.0 ppm), and $[\text{Mg}(\text{DCA})_4(\text{H}_2\text{O})_2]^{2-}$ (-43.2 ppm), see Fig. 2, 3 and Table 1. Assuming that this assignment is correct, it is possible to estimate the equilibrium constants in EMIM-DCA for:



consistently reproducing the data in Fig. 2 and 3. For Mg^{2+} in EMIM-Ac, only minor differences in chemical shift are observed experimentally, Fig. 2 and 3, in agreement with the small changes calculated when replacing acetate with water in the first coordination sphere, see Table 1. Thus, the resonances observed for EMIM-Ac may originate from $[\text{Mg}(\text{Ac})_4(\text{H}_2\text{O})_2]^{2-}$ (-38.1 ppm), and $[\text{Mg}(\text{Ac})_2(\text{H}_2\text{O})_4]$ (-31.9 ppm) or other complexes with mixed acetate and water coordination.

Interestingly, the calculated electric field gradients, V_{zz} , are very small for the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Mg}(\text{Ac})_4(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Mg}(\text{DCA})_6]^{4-}$ complexes. For $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mg}(\text{DCA})_6]^{4-}$, this is expected due to the high symmetry of the complex, *i.e.* these complexes may essentially escape quadrupolar line broadening. The remaining complexes are likely to experience quadrupolar line broadening of the conventional ^{25}Mg NMR reso-

Table 1 Calculated spectroscopic properties of selected complexes. Calculations were done at the B3LYP/pcSseg-2//B3LYP/pc-2 level with an iefpcm solvent model and a static dielectric constant of 11.7 corresponding to EMIM-DCA.^{32–36} Isotropic shielding, σ , chemical shift $\delta = (\sigma_{\text{ref}} - \sigma)/(1 - \sigma_{\text{ref}})$, arbitrarily with respect to $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, and electric field gradient, V_{zz} and η . See the ESI for details

Complex (in solvent with $\epsilon = 11.7$)	σ/ppm	δ/ppm	$^{25}\text{Mg}^a$	$^{31}\text{Mg}^a$	V_{zz} a.u.	η
			$\delta^{\text{expt}}/\text{ppm}$	$\delta^{\text{expt}}/\text{ppm}$		
$[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$	577	0			0.00	—
$[\text{Mg}(\text{DCA})_2(\text{H}_2\text{O})_4]$	578	-1			0.18	0.04
$[\text{Mg}(\text{DCA})_3(\text{H}_2\text{O})_3]^-$	581	-4			-0.12	0.87
$[\text{Mg}(\text{DCA})_4(\text{H}_2\text{O})_2]^{2-}$	585	-8		-43.2	-0.12	0.00
$[\text{Mg}(\text{DCA})_5(\text{H}_2\text{O})]^{3-}$	589	-12		-52.0	-0.04	0.22
$[\text{Mg}(\text{DCA})_6]^{4-}$	597	-20		-60.2	0.00	—
$[\text{MgCl}_2(\text{DCA})_2(\text{H}_2\text{O})_2]^{2-}$	573	4	-13.3		0.16	0.66
$[\text{Mg}(\text{Ac})_2(\text{H}_2\text{O})_4]$	570	7		-31.9	0.18	0.40
$[\text{Mg}(\text{Ac})_4(\text{H}_2\text{O})_2]^{2-}$	573	4	10.2	-38.1	-0.01	0.41

^a Experimental chemical shifts, assuming the indicated assignment (the absolute values of the chemical shifts differ because different chemical shift references were used).



nances. Although there are other contributions to the line width, this suggests that only the $[\text{Mg}(\text{Ac})_4(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Mg}(\text{DCA})_6]^{4-}$ complexes are readily observable in ^{25}Mg NMR, in agreement with the fact that only two resonances are observed. Moreover the observed chemical shift difference is ~ 23 ppm, see Fig. 2, Table 1, and Table S5.†

In summary, we have successfully recorded ^{31}Mg β -NMR spectra for Mg^{2+} in solution. Contrary to ^{25}Mg ($I = 5/2$), ^{31}Mg ($I = 1/2$) NMR spectra do not suffer from line broadening due to nuclear quadrupole interactions, and the sensitivity of ^{31}Mg β -NMR is far superior to that of ^{25}Mg NMR illustrating that β -NMR allows for interrogation of elements that are otherwise difficult or impossible to observe by NMR spectroscopy. The excellent resolution of the ^{31}Mg β -NMR spectra, allows for the discrimination of various complexes with the typical oxygen and nitrogen coordination formed by Mg^{2+} , and consequently opens for further characterization of the coordination chemistry of this spectroscopically elusive metal ion in solution. Finally, the results indicate that similar success may be achieved with application of β -NMR to other metal ions. Even formation of transient species and surface properties of liquids may be explored, as the time from implantation to measurement is of the order of a second, and the implantation depth can be controlled by the energy of the ion beam if diffusion is slow. Therefore, broader applications of β -NMR in inorganic and bioinorganic chemistry may be anticipated.

Conflicts of interest

There are no conflicts to declare.

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