Synthesis and characterization of magnetic ionic liquids containing multiple paramagnetic lanthanide and transition metal centers and functionalized diglycolamide ligands

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Abstract

Magnetic ionic liquids (MILs) containing paramagnetic centers have gained widespread recognition as sustainable solvents due to their ability to respond to an external magnetic field. The physico-chemical properties of MILs are dependent on the choice of anion/cation ligands and metal centers; the search for highly tunable ligands and precursors that can confer favorable characteristics, such as low viscosity, is ongoing. Diglycolamides employed as cationic ligands have been previously shown to form hydrophobic MILs that can simultaneously incorporate multiple lanthanide metal centers in both the anion/cation. Despite their enhanced magnetic susceptibility, the effect of diglycolamide chemical structure modifications on the physico-chemical properties of MILs has not been thoroughly studied. Additionally, the possibility of forming diglycolamide-based MILs with popularly employed transition metals has not been investigated and combinations that can simultaneously embed two different types of metal centers in both the anion/cation have not been explored. In this study, thirty (30) MILs comprised of lanthanide and transition metals were synthesized by examining their chelation to both straight-chained and branched diglycolamides. Transition metal-based MILs were found to possess high thermal stabilities up to 235 °C compared to 192 °C for those comprised of lanthanides. While MILs comprised of rare-earth metal centers exhibited the lowest viscosities, substituting lanthanides with transition metals in just the anion or cation resulted in enhanced thermal stability and reduced viscosity. The effective magnetic moment for these MILs varied between 4.71 and 21.08 μ_B and was much higher compared to all previous classes of MILs prepared using the same metals. Results from this study explore all possible modifications that can be made to these MILs in an effort to demonstrate their structural tunability, which is often highly desirable in various applications, including organic synthesis and chemical separations.

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1. Introduction

Ionic liquids (ILs) are molten salts that are popularly employed as designer solvents due to their tunable properties [1], [2], [3]. They are typically comprised of organic cations and paired with weakly coordinating anions to yield ionic compounds that melt below 100 °C [4], [5], [6]. Key characteristics of ILs include high chemical and thermal stability [7], [8], high electrical conductivity [9], [10], negligible vapor pressure [11], [12], and tunable viscosity [13], [14], making them highly desirable in catalysis [15], [16], synthesis [17], [18], and chemical separations [19], [20]. Magnetic ionic liquids (MILs) are a subcategory of ILs comprised of a paramagnetic center embedded within the cation and/or anion [21], [22], [23]. MILs have similar physico-chemical properties to ILs and can additionally respond to an external magnetic field, allowing them to be easily manipulated in any matrix using a neodymium rod magnet [20], [24].

Over the years, several classes of MILs have evolved owing to advancements made in their structural design and chemical composition [20], [25]. The first reported MIL was 1-butyl-3-methylimidazolium tetrachloroferrate(III) ($[C_4mim^+][FeCl_4^-]$) which incorporated the paramagnetic center in the anion [26]. Since then, other types of cations such as trihexyl(tetradecyl)phosphonium ($[P_{66614}^+]$) have been shown to form MILs with anions such as tetrachloromanganate(II) ($[MnCl_4^{2-}]$), tetrachlorocobalate(II) ($[CoCl_4^{2-}]$), gadolinium hexachloride ($[GdCl_6^{3-}]$), and $[FeCl_4^-]$ [25], [27]. However, these MILs were found to possess certain drawbacks. For example, MILs comprised of the $[FeCl_4^-]$ anion are prone to hydrolysis in water [28], [29] while $[P_{66614}^+]_2[MnCl_4^{2-}]$, $[P_{66614}^+]_2[CoCl_4^{2-}]$, and $[P_{66614}^+]_3[GdCl_6^{3-}]$ MILs have viscosities as high as 123,500 cP between 273 and 373 K [25], thereby limiting their usefulness in many applications. To address this, anions comprised of both transition and lanthanide metal centers chelated with hexafluoroacetylacetonate ligands ([hfacac$^-$]) were paired with the [P_{66614}^+] cation to form MILs possessing improved chemical stability and lower viscosity [29]. These results demonstrate that certain anion/cation combinations form MILs with highly desirable characteristics.

Fundamental research primarily focused on understanding the chemical structure of MILs aids in identifying key features that can impact specific MIL properties [30], [31], [32]. For example, bulky alkyl substituents in both the anion or cation can enhance MIL hydrophobicity while employing substituents such as the trifluoromethyl functional group (CF_3) in anion ligands can promote hydrophobicity and reduce MIL viscosity [20], [33]. Incorporating methyl, phenyl, biphenyl, and thienyl substituents in ligands has been found to influence both the viscosity and thermal stability of MILs comprised of [hfacac$^-$] metal chelates as anions [34]. Additionally, the type of paramagnetic center has been shown to impact their viscosity, magnetic susceptibility, as well as solvation properties [29], [35]. Clearly, both the type of ligands and paramagnetic centers forming the anion/cation can significantly influence the physico-chemical properties of MILs. However, the structural tunability of most classes of MILs is generally limited. Popular cations comprised of ammonium, imidazolium, and phosphonium derivatives predominantly differ in the length of their alkyl substituents and are devoid of polar functional groups [36], [37]. Among the very few types of MILs that employ a paramagnetic center in the cation are those comprised of N-substituted imidazole ligands, which may be modified to incorporate polar substituents [33]. However, these cations are comprised of monodentate ligands that may interact less strongly with metal centers compared to those composed of multidentate chelating species [38]. In addition, most classes of MILs incorporate a single paramagnetic center in either the cation or anion, thereby eliminating the possibility of simultaneously employing multiple metal centers to modulate their magnetic susceptibility and other physico-chemical properties.

Recently, a new class of MILs comprised of [hfacac$^-$] metal chelates was reported that simultaneously incorporates multiple paramagnetic centers in both the anion and cation [39]. However, only one type of ligand (i.e., N,N,N',N'-tetraoctyl diglycolamide or TODGA) has been employed in the cation and both the anion/cation were shown to incorporate only lanthanide metals. Additionally, viscosities and miscibility with organic solvents of these MILs have not been thoroughly investigated. The ability to structurally tune both the anion/cation with multidentate ligands possessing polar functional groups and alkyl substituents provides tremendous potential to modulate MIL properties. More importantly, developing transition metal-based derivatives of these MILs has the potential to expand their scope to a diverse variety of applications as many of these preferably employ MILs composed of cobalt (Co), nickel (Ni) and manganese (Mn) metals [22], [40]. Furthermore, MIL combinations comprised of 2 different types of paramagnetic centers in the anion/cation can be prepared, thereby incorporating characteristics of both metals.

In this study, thirty (30) MILs comprised of paramagnetic centers in both the anion and cation were synthesized and their viscosities, magnetic susceptibility and thermal properties were thoroughly investigated. For the first time, transition metals were shown to coordinate with TODGA to form cations which were paired with [hfacac$^-$] metal chelates. Three additional derivatives of TODGA were employed in the cation component to investigate the effect of short as well as branched alkyl chain substituents on the physico-chemical properties of these MILs. Magnetic susceptibility, viscosity, and thermal stability of the MILs were thoroughly characterized and benchmarked against those comprised of lanthanide metal centers. Additionally, MIL combinations that can simultaneously incorporate 2 different types of paramagnetic centers in the cation/anion were also explored. Effective magnetic moments (μ_{eff}) of MILs generated in this study varied between 4.71 and 21.08 Bohr magnetons (μ_{B}) and were found to be solely dependent on the type of paramagnetic centers. The choice of cation ligand within the MIL significantly influenced the observed thermal stability of the MILs and those comprised of straight-chained octyl substituents were found to be stable at temperatures up to 235 °C. This study demonstrates versatility in the design and synthesis of these MILs and thoroughly explores their structural tunability, thus making their use highly appealing in a diverse range of applications involving chemical and electrochemical separations, catalysis, and organic synthesis.

2. Experimental

2.1. Instrumentation

Nuclear magnetic resonance (NMR) spectroscopy was performed using Bruker 400 and 600 MHz spectrometers. A Thermo Scientific FlashSmart 2000 CHNS/O Combustion Elemental Analyzer (Waltham, MA, USA) was employed to perform elemental analysis. Viscosity measurements were performed at 19.9 °C using a Brookfield DV1 cone and plate viscometer equipped with a CPA-51Z cone spindle. Approximately, 0.5 g of each MIL was used to record its viscosity after being extensively dried for 48 hours under vacuum. Magnetic susceptibility measurements were obtained using a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS XL-7) and a magnetic susceptibility balance (MSB, Sherwood Scientific, Cambridge, UK). Thermal stability studies of MILs were measured using gas chromatography by treating them as a thin film chromatographic stationary phase and subjecting them to a temperature program. MILs were dissolved in dichloromethane to prepare coating solutions at a concentration of 0.32% w/v. Five-meter segments of untreated fused silica capillary were filled with these solutions and sealed at one end. The other end of the capillary was connected to a vacuum and then placed in a water bath maintained at 40 °C to facilitate coating of the MIL on the inner wall of the capillary columnn. All MILs were coated at an approximate film thickness of 0.20 µm [41]. An Agilent 6890N gas chromatograph fitted with a flame ionization detector (FID) was employed for thermal stability measurements and all chromatographic columns were conditioned at 40 °C under a constant flow of helium (1 mL min^{-1}) with the inlet/detector temperature maintained at 150 °C. An oven temperature program from 40 to 240 °C with an incremental heating rate of 1 °C min^{-1} was employed to record the FID detector response as a function of temperature.

2.2. Ligand preparation and characterization

A comprehensive list of reagents, starting materials, and their purities can be found in the supporting information. All cation ligands (tetraalkyl diglycolamides) were synthesized using a reaction scheme reported elsewhere [42]. Diglycolyl chloride (20 mmol) was placed in a 250 mL round bottom flask and dissolved in 50 mL of diethyl ether. A mixture of triethylamine (90 mmol) and 40 mmol of a dialkylamine (dioctylamine, dibutylamine, diisobutylamine, or di-2-ethylhexylamine) was added dropwise to the contents of the flask and stirred for 5 hours under ambient conditions. The resulting solution was washed 3 times with 30 mL of 10% HCl solution followed by water in a 250 mL separatory funnel. The organic layer was then washed with 50 mL of 5% (w/w) $NaHCO_3$ solution, dried over $MgSO_4$, and subsequently filtered under gravity. Diethyl ether was removed under reduced pressure and the products were dried under vacuum for 2 days. The following tetraalkyl diglycolamides were synthesized and characterized using ^{13}C and ^{1}H NMR (spectra provided in the supporting information):

NMR analysis of N,N,N’,N’-tetrabutyl diglycolamide (TBDGA): A yellow liquid. Yield of 83%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.30 (s, 4H), 3.35 – 3.24 (m, 4H), 3.23 – 3.12 (m, 4H), 1.56 – 1.44 (m, 8H), 1.29 (h, *J* = 7.4 Hz, 8H), 0.91 (q, *J* = 7.3 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.49, 69.06, 46.66, 45.47, 31.01, 29.68, 20.19, 20.01, 13.84, 13.79, 13.70.

NMR analysis of N,N,N’,N’-tetraisobutyl diglycolamide (iTBDGA): A yellow liquid. Yield of 81%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.31 (s, 4H), 3.16 (d, *J* = 7.6 Hz, 4H), 3.01 (d, *J* = 7.7 Hz, 4H), 1.97 (hept, *J* = 6.9 Hz, 2H), 1.86 (dp, *J* = 13.9, 6.8 Hz, 2H), 0.84 (dd, *J* = 12.0, 6.7 Hz, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.36, 68.89, 53.96, 52.40, 27.32, 26.21, 20.09, 19.87.

NMR analysis of N,N,N’,N’-tetraoctyl diglycolamide (TODGA): A yellow liquid. Yield of 87%. ^{1}H NMR (400 MHz, $cdcl_3$) δ 4.31 (s, 3H), 3.34 – 3.22 (m, 4H), 3.22 – 3.09 (m, 4H), 1.60 – 1.43 (m, 8H), 1.33 – 1.18 (m, 40H), 0.86 (td, *J* = 6.8, 3.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.45, 77.27, 69.09, 46.92, 45.76, 31.80, 31.75, 29.51, 29.36, 29.32, 29.24, 29.20, 28.96, 28.79, 27.60, 27.41, 27.16, 27.03, 26.99, 26.96, 26.82, 22.66, 22.63, 22.61, 14.07, 14.05.

NMR analysis of N,N,N’,N’-(2-ethylhexyl) diglycolamide (TEHDGA): A yellow liquid. Yield of 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (s, 2H), 3.39 – 3.16 (m, 2H), 3.09 (d, *J* = 7.5 Hz, 2H), 2.46 (d, *J* = 6.2 Hz, 3H), 1.67 (p, *J* = 6.5 Hz, 1H), 1.55 (d, *J* = 6.3 Hz, 1H), 1.45 – 1.36 (m, 2H), 1.35 – 1.15 (m, 31H), 0.97 – 0.77 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.56, 77.25, 69.19, 53.55, 49.99, 47.86, 47.82, 39.43, 39.26, 37.91, 36.66, 31.42, 30.54, 30.48, 28.99, 28.82, 28.81, 28.71, 28.68, 24.54, 23.79, 23.75, 23.14, 23.08, 23.01, 14.12, 14.08, 14.02, 10.93, 10.87, 10.61, 10.59.

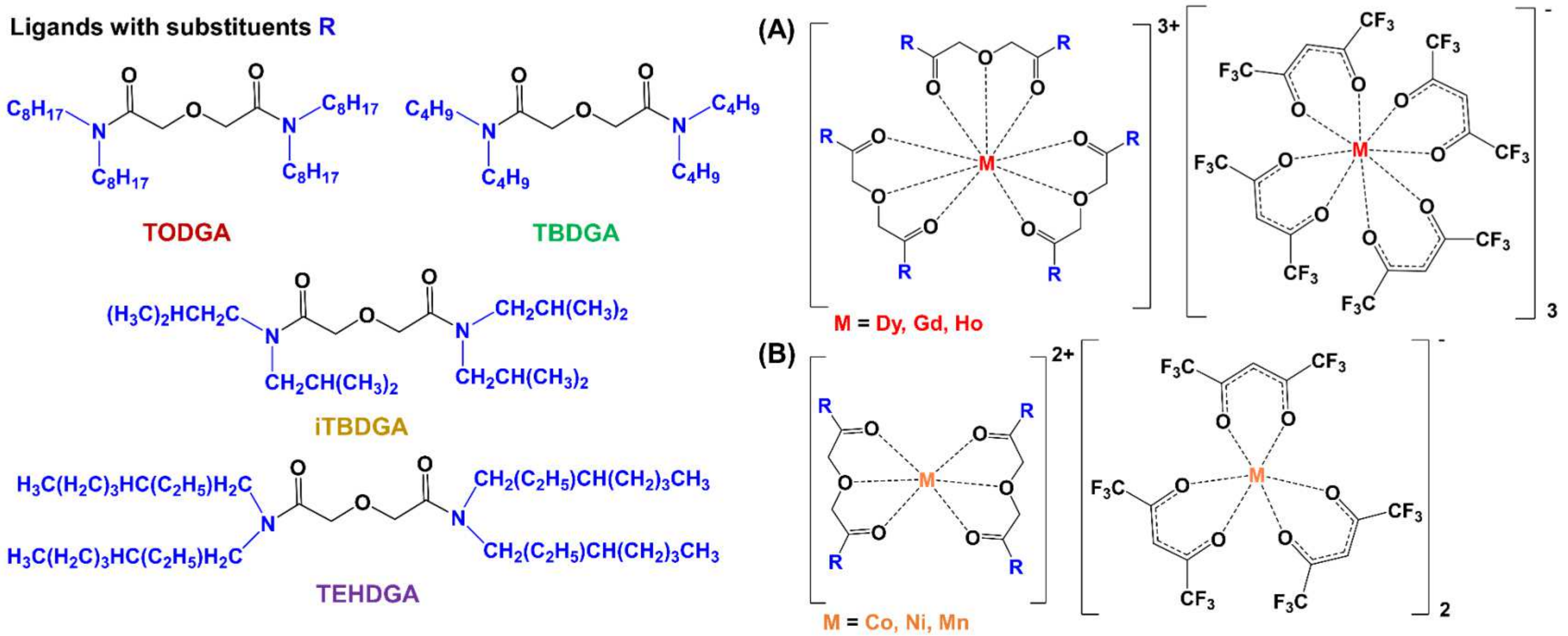
2.3. MIL preparation and characterization

All MILs were prepared using a modified version of a previously reported reaction scheme [39]. Tetraalkyl diglycolamides were dissolved in 50 mL of methanol and reacted overnight with metal chlorides ($CoCl_2$, $NiCl_2$, and $MnCl_2.4H_2O$) in a 2:1 molar ratio to form transition metal-based chloride salts of the cation. Methanol was removed under reduced pressure and the product dissolved in 40 mL of diethyl ether and washed with 10 mL of water several times until the aqueous layer formed no precipitate when mixed with $AgNO_3$. Diethyl ether was evaporated under reduced pressure and the cation salt was dried under vacuum for 2 days. Anion salts comprised of [hfacac$^-$] metal chelates were prepared according to a previously reported procedure [29]. Transition metal-based MILs containing the same metal center in both the anion and cation (homogenous MIL combinations) were prepared by reacting their cation salts overnight with [hfacac$^-$] metal chelates in a 1:2 molar ratio using 40 mL of acetonitrile as the reaction medium. The solvent was removed under reduced pressure and the product was dissolved in 40 mL of diethyl ether and washed with 10 mL of water repeatedly until the aqueous layer yielded no precipitate when mixed with $AgNO_3$. Diethyl ether was evaporated under reduced pressure and the final MIL was dried under vacuum for 48 hours prior to further analysis. To prepare lanthanide metal-based chloride salts of the cation, tetraalkyl diglycolamides were reacted with metal chlorides ($DyCl_3.6H_2O$, $GdCl_3.6H_2O$, and $HoCl_3.6H_2O$) in a 3:1 molar ratio using the same procedure as described above. Additionally, their cation salts were reacted with [hfacac$^-$] metal chelates in a 1:3 molar ratio. Homogenous MIL combinations comprised of identical paramagnetic centers with different tetraalkyl diglycolamides were prepared, as shown in Figure 1 (MIL **1** to **24**).

In addition, heterogenous MIL combinations comprised of different metal centers in the cation and anion were prepared, as shown in Figure 2 (MIL **25** to **30**). MIL **25** was prepared by reacting the cobalt-containing cation salt with [hfacac$^-$] metal chelate of nickel in a 1:2 molar ratio while MIL **26** was synthesized by pairing the cation salt of nickel metal with [hfacac$^-$] metal chelate of cobalt in the same molar ratio. In contrast, MILs **27** and **28** were prepared by reacting the cation salt of dysprosium with [hfacac$^-$] metal chelates of cobalt and nickel in a 1:3 molar ratio, respectively. Lastly, MILs **29** and **30** were obtained by reacting the [hfacac$^-$] metal chelate of dysprosium with cations comprised of nickel and cobalt in a 2:1 molar ratio, respectively. The purity of all MILs was characterized using carbon, hydrogen, and nitrogen (CHN) elemental analysis and a comparison of experimental data with theoretical values can be found in the supporting information.

3. Results and discussion

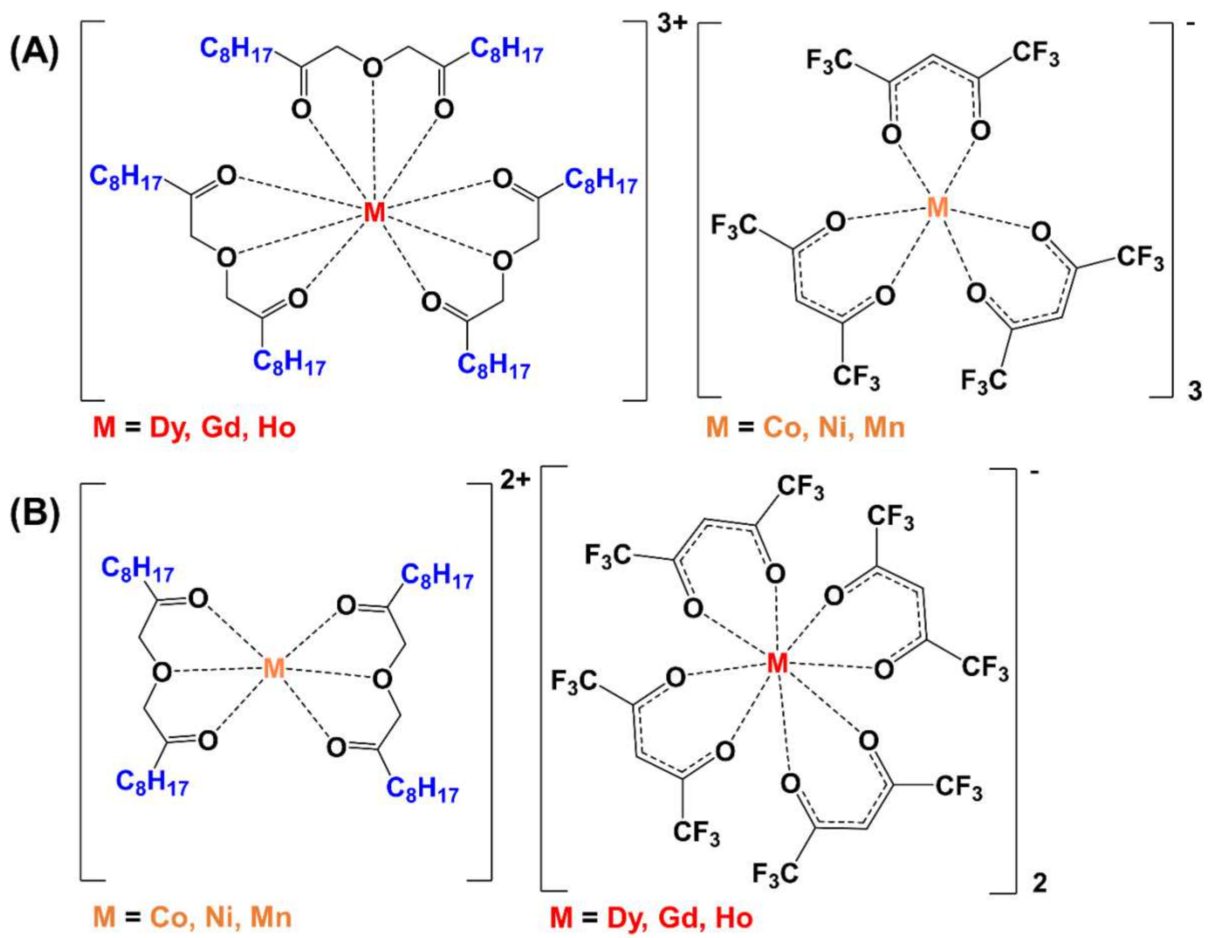
The structural tunability of MILs has been a subject of key interest in the fields of catalysis [15], [16], organic synthesis [12], [17], and extractions [22], [27]. The cation/anion structures can be modulated for specific applications and certain types of MILs are better suited for a particular purpose. For example, it has been reported that DNA can interact with MILs via π-π stacking, hydrogen bonding, and dispersive-type interactions [22], [40]. Consequently, MILs that can interact strongly by these solvation interactions are often best suited for extracting DNA from complex matrices. In developing an *in situ* dispersive liquid-liquid microextraction technique for DNA extraction, Bowers et al. showed that MILs comprised of N-substituted imidazole ligands incorporating the benzyl functional group resulted in higher extraction efficiencies due to stronger π-π interactions compared to those possessing butyl and octyl substituents [22]. In contrast, acetylacetonate-based MILs were chosen as ideal candidates for rapid nucleic acid quantification using real-time polymerase chain reaction as these did not inhibit DNA amplification [40]. While new classes of MILs that combine structural features of both the acetylacetonate [29] and imidazole-based [33] MILs appear promising due to enhanced magnetic properties [39], their true potential in catalysis, chemical separations, and organic synthesis cannot be exploited unless versatility in their design and synthesis is fully understood. Currently, no study exists that explores all possible structural modifications that can be imparted to these MILs and their impact on overall physico-chemical properties. Therefore, this work thoroughly investigates the physico-chemical properties of these MILs by modulating both the type of ligands and the metal centers employed in the cation/anion. In addition, transition metals have also been incorporated into the anion/cation for the first time to expand the choice of MIL combinations within this class.



Homogenous MIL combinations

1. [Co(TODGA)$_2$][Co(hfacac)$_3$]$_2$
2. [Ni(TODGA)$_2$][Ni(hfacac)$_3$]$_2$
3. [Mn(TODGA)$_2$][Mn(hfacac)$_3$]$_2$
4. [Dy(TODGA)$_3$][Dy(hfacac)$_4$]$_3$
5. [Gd(TODGA)$_3$][Gd(hfacac)$_4$]$_3$
6. [Ho(TODGA)$_3$][Ho(hfacac)$_4$]$_3$
7. [Co(TBDGA)$_2$][Co(hfacac)$_3$]$_2$
8. [Ni(TBDGA)$_2$][Ni(hfacac)$_3$]$_2$
9. [Mn(TBDGA)$_2$][Mn(hfacac)$_3$]$_2$
10. [Dy(TBDGA)$_3$][Dy(hfacac)$_4$]$_3$
11. [Gd(TBDGA)$_3$][Gd(hfacac)$_4$]$_3$
12. [Ho(TBDGA)$_3$][Ho(hfacac)$_4$]$_3$
13. [Co(TEHDGA)$_2$][Co(hfacac)$_3$]$_2$
14. [Ni(TEHDGA)$_2$][Ni(hfacac)$_3$]$_2$
15. [Mn(TEHDGA)$_2$][Mn(hfacac)$_3$]$_2$
16. [Dy(TEHDGA)$_3$][Dy(hfacac)$_4$]$_3$
17. [Gd(TEHDGA)$_3$][Gd(hfacac)$_4$]$_3$
18. [Ho(TEHDGA)$_3$][Ho(hfacac)$_4$]$_3$
19. [Co(iTBDGA)$_2$][Co(hfacac)$_3$]$_2$
20. [Ni(iTBDGA)$_2$][Ni(hfacac)$_3$]$_2$
21. [Mn(iTBDGA)$_2$][Mn(hfacac)$_3$]$_2$
22. [Dy(iTBDGA)$_3$][Dy(hfacac)$_4$]$_3$
23. [Gd(iTBDGA)$_3$][Gd(hfacac)$_4$]$_3$
24. [Ho(iTBDGA)$_3$][Ho(hfacac)$_4$]$_3$

Figure 1: Chemical structures and numbering scheme used for homogenous MIL combinations examined in this study. Abbreviations: N,N,N’,N’-tetraoctyl diglycolamide (TODGA), N,N,N’,N’-tetrabutyl diglycolamide (TBDGA), N,N,N’,N’-tetraisobutyl diglycolamide (iTBDGA), and N,N,N’,N’-(2-ethylhexyl) diglycolamide or (TEHDGA). (A) Structure of a lanthanide MIL and (B) transition metal-based MIL.



Heterogenous MIL combinations

25. $[Co(TODGA)_2][Ni(hfacac)_3]_2$
26. $[Ni(TODGA)_2][Co(hfacac)_3]_2$
27. $[Dy(TODGA)_3][Co(hfacac)_3]_3$
28. $[Dy(TODGA)_3][Ni(hfacac)_3]_3$
29. $[Ni(TODGA)_2][Dy(hfacac)_4]_2$
30. $[Co(TODGA)_2][Dy(hfacac)_4]_2$

Figure 2: Abbreviations, chemical structures, and numbering scheme employed for heterogenous MIL combinations. (A) Structure of a MIL incorporating lanthanides in the cation and a transition metal in the anion and (B) a MIL containing transition metal centers in the cation and rare-earth metals in the anion.

The cation ligands and metal centers employed in this study were carefully chosen to explore different structural changes that can be introduced to these MILs. Figure 1 shows the 4 cationic ligands (TODGA, TBDGA, iTBDGA, and TEHDGA) that were employed. TODGA and TBDGA were used to investigate the effect of varying the length of alkyl chain substituents in the cation while TEHDGA and iTBDGA demonstrated the impact of using branched ligands. With each cationic ligand, 6 different metal centers (Co, Ni, Mn, Dy, Gd, Ho) were coordinated to synthesize 24 homogenous MIL combinations where both the anion and cation incorporated the same metal centers. Any observed differences in physico-chemical properties can be attributed to the nature of the metal centers. While the lanthanide-based MILs has been previously reported [39], the coordination of diglycolamide-based cationic ligands with transition metals is studied for the first time here. Figures 1A and 1B compare the structure of lanthanide and transition metal-based MILs, respectively. Elemental analysis of transition metal-based MILs revealed that only 2 cationic ligands were coordinated with the metal centers compared to 3 ligands in those comprised of lanthanides (see supporting information). In contrast to 4 hexafluoroacetylacetonate ligands coordinated to lanthanide metals in the anion (Figure 1A), only 3 ligands interacted with the transition metal centers (Figure 1B). Clearly, these significant differences in MIL structure between lanthanide and transition metal-based MILs formed the basis of variations between their physico-chemical properties.

Given that both the anion and cation contain metal centers, the possibility of having two different paramagnetic centers in a MIL is appealing. Incorporating two different transition metals or lanthanides could integrate the characteristics of both metals into the chemical structure and composition of a single MIL. Since the number of ligands in lanthanide and transition metal-based MILs was observed to be different, having one transition metal and one lanthanide embedded into the MIL chemical structure could incorporate the characteristics of two different classes of metal centers while further varying the geometry of the anion and cation. Figure 2 shows six heterogenous MIL combinations that were prepared using the TODGA ligand. MILs **25** and **26** employed two different transition metals in the anion/cation. The structure of these two MILs are the same as the one shown in Figure 1B. In contrast, MILs **27** and **28** (Figure 2) incorporated a lanthanide in the cation and a transition metal in the anion. The opposite was observed for MILs **29** and **30** that employed a transition metal center in the cation and a lanthanide in the anion. The structure of MILs **27** and **28** is shown in Figure 2A while Figure 2B resembles MILs **29** and **30**.

3.1. Thermal stability

The ability of ILs and MILs to withstand high temperatures can facilitate their use in certain applications. In MILs comprised of the [P_{66614}^{+}] cation with [$hfacac^{-}$] metal chelates, the thermal stability is limited due to weak metal-ligand interactions [29]. However, incorporating aromatic functional groups, such as phenyl, naphthyl, and thiophenyl moieties, results in derivatives of the same class of MILs that have been shown to possess enhanced thermal stabilities ranging between temperatures of 230 and 260 °C [34]. It was further revealed that manganese-containing MILs were more thermally robust (155 °C) compared to those comprised of cobalt metal (130 °C) while neodymium-based MILs possessed the highest thermal stability with a gradual degradation observed at 225 °C [29]. Clearly, variations in thermal stability amongst lanthanide and transition metal-based MILs within the same class necessitates thorough investigation. Since the MILs employed in this study consist of metal-ligand interactions in both the anion and cation, it is vital that their thermal stability is benchmarked against previous classes of MILs comprised of [$hfacac^{-}$] metal chelates.

To measure the thermal stability of MILs with enhanced sensitivity and greater precision, the MIL was coated on the inner wall of a capillary column and subjected to a gas chromatography (GC) heating rate of 1 °C min^{-1}. While temperature ramp rates of 5 °C min^{-1} are normally employed in thermogravimetric analysis, a lower heating rate employed in GC enabled the precise identification of the onset of MIL volatilization as a function of temperature. Figure 3 demonstrates the flame ionization detector response as the MIL began to volatilize/decompose/degrade, these products were detected as a function of temperature for select MILs. The effect of varying alkyl substituents within the cationic ligands is shown in Figure 3A. It was observed that the $[Dy(TBDGA)_3][Dy(hfacac)_4]_3$ and $[Dy(iTBDGA)_3][Dy(hfacac)_4]_3$ MILs produced higher thermal decomposition compared to the $[Dy(TODGA)_3][Dy(hfacac)_4]_3$ and $[Dy(TEHDGA)_3][Dy(hfacac)_4]_3$ MILs, indicating stronger metal-ligand interactions for those comprised of octyl substituents. A comparison of the $[Dy(TBDGA)_3][Dy(hfacac)_4]_3$ MIL to the $[Dy(iTBDGA)_3][Dy(hfacac)_4]_3$ MIL and the $[Dy(TODGA)_3][Dy(hfacac)_4]_3$ MIL to $[Dy(TEHDGA)_3][Dy(hfacac)_4]_3$ MIL suggests that branched cationic ligands offer higher thermal stabilities compared to straight-chain analogs. Table 1 provides the onset temperature of MIL volatilization/decomposition where it can be observed that isomers of the octyl substituents (MILs **4** and **16**) resulted in thermal degradation at temperatures of 175 and 152 °C, respectively, compared to 135 and 138 °C for those comprised of butyl functional groups (MILs **10** and **22**, respectively). Figure 3B compares the thermal stabilities of lanthanide and transition metal-based MILs. Higher thermal degradation was observed for $[Dy(TODGA)_3][Dy(hfacac)_4]_3$ (MIL **4**, red line) and $[Ho(TODGA)_3][Ho(hfacac)_4]_3$ (MIL **6**, black line) compared to MIL **1** ($[Co(TODGA)_2][Co(hfacac)_3]_2$) and MIL **2** ($[Ni(TODGA)_2][Ni(hfacac)_3]_2$) represented by the orange and grey plots, respectively. In addition, stronger interactions were observed between ligands and transition metal centers as MILs **1** and **2** degraded at significantly higher temperatures of 231 and 235 °C, respectively, compared to 175 °C for MIL **4** and 192 °C for MIL **6**.

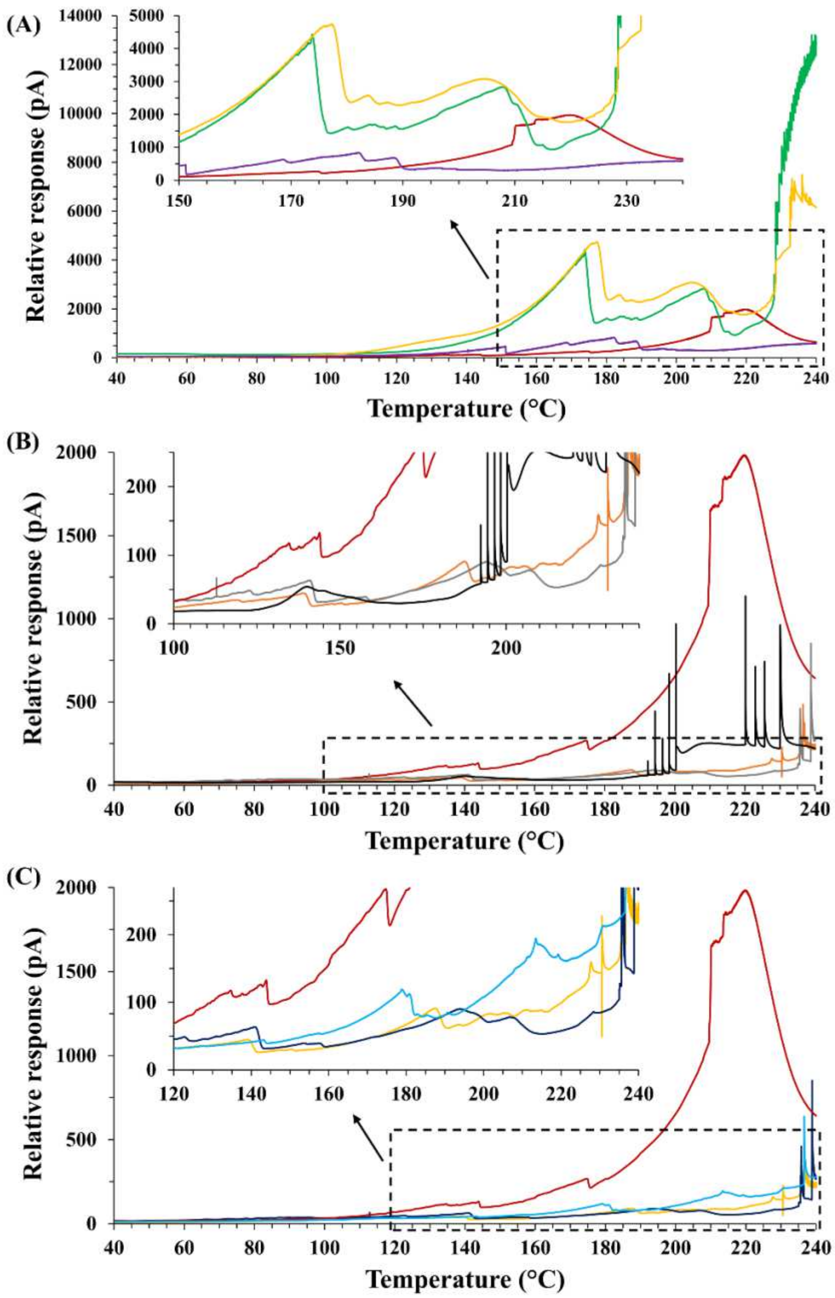


Figure 3: Thermal stability diagram for lanthanide and transition metal-based MILs obtained by recording the detector response of a GC-FID as a function of temperature: $[Dy(TODGA)_3][Dy(hfacac)_4]_3$ (—); $[Dy(TBDGA)_3][Dy(hfacac)_4]_3$ (—); $[Dy(TEHDDGA)_3][Dy(hfacac)_4]_3$ (—); $[Dy(iTBDGA)_3][Dy(hfacac)_4]_3$ (—); $[Ho(TODGA)_3][Ho(hfacac)_4]_3$ (—); $[Co(TODGA)_2][Co(hfacac)_3]_2$ (—); $[Ni(TODGA)_2][Ni(hfacac)_3]_2$ (—); $[Dy(TODGA)_3][Co(hfacac)_3]_3$ (—); $[Dy(TODGA)_3][Ni(hfacac)_3]_3$ (—); and $[Dy(TODGA)_3][Mn(hfacac)_3]_3$ (—). (A) Effect of cationic ligands, (B) comparison of lanthanide and transition metal-based MILs, and (C) heterogenous MIL combinations comprised of dysprosium-based cations and transition metals in the anion.

Table 1. Viscosity data obtained at 19.9 °C and decomposition/degradation temperatures for lanthanide and transition metal-based MILs comprised of TODGA and its derivatives.

MIL No.	MIL abbreviation	Viscosity (cP)	Onset of MIL volatilization (°C)	Reference
1	**$[Co(TODGA)_2][Co(hfacac)_3]_2$**	28,310	231	Present work
2	**$[Ni(TODGA)_2][Ni(hfacac)_3]_2$**	33,830	235	Present work
4	**$[Dy(TODGA)_3][Dy(hfacac)_4]_3$**	9,210	175	Present work
5	**$[Gd(TODGA)_3][Gd(hfacac)_4]_3$**	13,640	183	Present work
6	**$[Ho(TODGA)_3][Ho(hfacac)_4]_3$**	10,530	192	Present work
10	**$[Dy(TBDGA)_3][Dy(hfacac)_4]_3$**	104,390	135	Present work
16	**$[Dy(TEHDGA)_3][Dy(hfacac)_4]_3$**	21,350	152	Present work
22	**$[Dy(iTBDGA)_3][Dy(hfacac)_4]_3$**	-	138	Present work
25	**$[Co(TODGA)_2][Ni(hfacac)_3]_2$**	21,410	223	Present work
26	**$[Ni(TODGA)_2][Co(hfacac)_3]_2$**	27,110	228	Present work
27	**$[Dy(TODGA)_3][Co(hfacac)_3]_3$**	25,980	237	Present work
28	**$[Dy(TODGA)_3][Ni(hfacac)_3]_3$**	29,550	238	Present work
-	**$[P_{66614}][Co(hfacac)_3]$**	575.8[a]	130	[29]
-	**$[P_{66614}][Ni(hfacac)_3]$**	927.9[a]	215	[29]
-	**$[P_{66614}][Mn(hfacac)_3]$**	401.8[a]	155	[29]
-	**$[P_{66614}]_3[GdCl_6]$**	28,230[b]	352[c]	[46]
-	**$[P_{66614}]_2[CoCl_4]$**	123,500[b]	373[c]	[46]
-	**$[P_{66614}]_2[MnCl_4]$**	112,300[b]	346[c]	[46]

[a] Viscosity measurement reported at 23.7 °C

[b] Viscosity measurement reported at 20.0 °C

[c] MIL degradation temperature measured using thermogravimetric analysis

In contrast, Figure 3C demonstrates that switching the lanthanide metal center in just the anion can significantly improve the thermal stability of these MILs. Compared to MIL **4**, the $[Dy(TODGA)_3][Co(hfacac)_3]_3$, $[Dy(TODGA)_3][Ni(hfacac)_3]_3$, and $[Dy(TODGA)_3][Mn(hfacac)_3]_3$ MILs exhibited significantly lower thermal degradation between 180 and 240 °C. Both homogenous and heterogenous MIL combinations of transition metals yielded a sharp spike in thermal decomposition at around 235 °C that was not observed in the case of lanthanides. Additionally, the onset of thermal degradation (Table 1) for transition metal-containing ILs (MILs **1** and **2**) and heterogenous combinations (MILs **25**-**28**) was measured to be between 223 and 238 °C, which was much higher compared to those comprised of lanthanides (MILs **4** and **6**). Most MILs appeared to degrade in successive steps as observed from the thermal stability diagram (Figure 3), irrespective of the type of ligand or metal center comprising them. It has been reported previously that MILs containing the $[hfacac^-]$ metal chelates decompose by a multi-step degradation process [34]. Given that both the cation and anion are comprised of metal chelates, these MILs gradually decomposed as metal-ligand interactions were evidently weakened with an increase in temperature.

3.2. Viscosity

The viscosity of ILs and MILs can influence their use in certain applications. For example, it has been reported that the conductivity of ILs is inversely related to their viscosity as it affects mass transport, which can significantly impact their effectiveness in electrochemical applications [43], [44], [45]. Despite being composed of the same paramagnetic center, MILs can possess a wide range of viscosities depending on their class. For example, a viscosity of 83,450 cP was reported for the $[P_{66614}^+]_2[CoCl_4^{2-}]$ MIL at 25 °C [46] while the $[P_{66614}^+][Co(hfacac)_3]_2$ MIL exhibits a lower viscosity of only 575.80 cP at 23.7 °C [29]. In MILs comprised of $[hfacac^-]$ metal chelates, incorporating phenyl moieties resulted in viscosities of up to 49,542 cP at 65 °C [34]. Given that the MILs explored in this study share the same type of anion, the choice of ligands was kept devoid of aromatic substituents in an attempt to form combinations featuring the lowest viscosities.

Viscosity measurements were performed under ambient conditions (19.9 °C) as MILs are often employed in applications without heating. Table 1 provides the viscosity data for select MIL combinations where it can observed that both the type of metal centers and cationic ligands significantly influence their fluidity. Compared to a value of 9,210 cP for the $[Dy(TODGA)_3][Dy(hfacac)_4]_3$ MIL, the viscosity of the $[Dy(TBDGA)_3][Dy(hfacac)_4]_3$ MIL was approximately 11.3 times higher (104,390 cP), demonstrating its significantly lower ability to flow for MILs comprised of cationic ligands possessing short alkyl substituents. In contrast to the $[Dy(TODGA)_3][Dy(hfacac)_4]_3$ MIL, the $[Dy(TEHDGA)_3][Dy(hfacac)_4]_3$ MIL exhibited a slightly higher viscosity of 21,350 cP, exemplifying the effect of branching in alkyl chain functional groups. Additionally, the $[Dy(iTBDGA)_3][Dy(hfacac)_4]_3$ MIL was observed to be a solid at room temperature compared to the $[Dy(TBDGA)_3][Dy(hfacac)_4]_3$ MIL, demonstrating higher melting point/glass transition temperatures for MILs comprised of branched ligands which was previously observed for imidazolium-based ILs [47]. In comparison to those MILs comprised of transition metals (MILs **1** and **2**), lanthanide-based MILs offered the lowest viscosities with values of 9,210, 13,640, and 10,530 cP for the $[Dy(TODGA)_3][Dy(hfacac)_4]_3$, $[Gd(TODGA)_3][Gd(hfacac)_4]_3$, and $[Ho(TODGA)_3][Ho(hfacac)_4]_3$ MILs. However, smaller differences in viscosity were observed within the same class of metal centers. For example, the $[Co(TODGA)_2][Co(hfacac)_3]_2$ and $[Ni(TODGA)_2][Ni(hfacac)_3]_2$ MILs possessed viscosities of 28,310 and 33,830 cP, keeping in line with literature evidence that the smaller atomic radius of nickel leads to shorter metal-ligand bond distances and a decrease in the size of the anion and enhanced MIL viscosity [29]. Heterogenous MIL combinations comprised of only transition metal centers (MILs **25** and **26**) resulted in significantly lower viscosities of 21,410 and 27,110 cP, respectively, compared to $[Co(TODGA)_2][Co(hfacac)_3]_2$ (MIL **1**) and $[Ni(TODGA)_2][Ni(hfacac)_3]_2$ (MIL **2**). In contrast, the $[Dy(TODGA)_3][Co(hfacac)_3]_3$ and $[Dy(TODGA)_3][Ni(hfacac)_3]_3$ MILs exhibited slightly higher viscosities of 25,980 and 29,550 cP, respectively, compared to MILs **25** and **26**. Clearly, these results demonstrate that this class of MILs can offer a diverse range of viscosities and that a suboptimal choice of ligands or metal centers can adversely impact them.

3.3. Solvent miscibility

In order to effectively employ MILs as solvents or reaction media in catalysis, organic synthesis, and chemical separations, it is essential to study their solubility in both polar and non-polar compounds. To gather a fundamental understanding of solvent properties of the MILs examined in this study, their miscibility with organic solvents was studied. To prepare a concentration of 10% (w/v) MIL-to-solvent ratio, 100 mg of each MIL was weighed out into a 20 mL glass vial and thoroughly mixed with 1 mL of the desired solvent by vigorously swirling the contents of the container. Table 2 provides the solubility of each MIL in 14 different solvents at various concentrations. MILs comprised of cationic ligands possessing longer alkyl substituents were found to dissolve better in non-polar solvents such as hexane and benzene up to concentrations of 20% (w/v) MIL-to-solvent ratio while branched ligands showed no solubility difference compared to straight-chained isomers. Transition metal-based MILs comprised of ligands featuring octyl substituents (MILs **1-3** and **13-15**) dissolved in hexane and benzene at a concentration of 10% (w/v) MIL-to-solvent ratio while those composed of butyl substituents (MILs **7-9** and **19-21**) were found to be insoluble.

Table 2. Solubility of lanthanide and transition metal-based MILs determined in 14 different solvents at 3 different concentrations.

MIL No.	MIL abbreviation	Solubility	MIL No.	MIL abbreviation	Solubility
1	**$[Co(TODGA)_2][Co(hfacac)_3]_2$**	$S^aS^bS^e$	**16**	**$[Dy(TEHDGA)_3][Dy(hfacac)_4]_3$**	$S^aS^bS^cS^e$
2	**$[Ni(TODGA)_2][Ni(hfacac)_3]_2$**	$S^aS^bS^c$	**17**	**$[Gd(TEHDGA)_3][Gd(hfacac)_4]_3$**	$S^aS^bS^cS^c$
3	**$[Mn(TODGA)_2][Mn(hfacac)_3]_2$**	$S^aS^bS^c$	**18**	**$[Ho(TEHDGA)_3][Ho(hfacac)_4]_3$**	$S^aS^bS^cS^c$
4	**$[Dy(TODGA)_3][Dy(hfacac)_4]_3$**	$S^aS^bS^cS^c$	**19**	**$[Co(iTBDGA)_2][Co(hfacac)_3]_2$**	$S^bS^dS^c$
5	**$[Gd(TODGA)_3][Gd(hfacac)_4]_3$**	$S^aS^bS^cS^e$	**20**	**$[Ni(iTBDGA)_2][Ni(hfacac)_3]_2$**	$S^bS^dS^e$
6	**$[Ho(TODGA)_3][Ho(hfacac)_4]_3$**	$S^aS^bS^cS^e$	**21**	**$[Mn(iTBDGA)_2][Mn(hfacac)_3]_2$**	$S^bS^dS^e$
7	**$[Co(TBDGA)_2][Co(hfacac)_3]_2$**	$S^bS^dS^e$	**22**	**$[Dy(iTBDGA)_3][Dy(hfacac)_4]_3$**	$S^aS^bS^e$
8	**$[Ni(TBDGA)_2][Ni(hfacac)_3]_2$**	$S^bS^dS^e$	**23**	**$[Gd(iTBDGA)_3][Gd(hfacac)_4]_3$**	$S^aS^bS^e$
9	**$[Mn(TBDGA)_2][Mn(hfacac)_3]_2$**	$S^bS^dS^e$	**24**	**$[Ho(iTBDGA)_3][Ho(hfacac)_4]_3$**	$S^aS^bS^e$
10	**$[Dy(TBDGA)_3][Dy(hfacac)_4]_3$**	$S^aS^bS^c$	**25**	**$[Co(TODGA)_2][Ni(hfacac)_3]_2$**	$S^aS^bS^c$
11	**$[Gd(TBDGA)_3][Gd(hfacac)_4]_3$**	$S^aS^bS^c$	**26**	**$[Ni(TODGA)_2][Co(hfacac)_3]_2$**	$S^aS^bS^c$
12	**$[Ho(TBDGA)_3][Ho(hfacac)_4]_3$**	$S^aS^bS^c$	**27**	**$[Dy(TODGA)_3][Co(hfacac)_3]_3$**	$S^aS^bS^c$
13	**$[Co(TEHDGA)_2][Co(hfacac)_3]_2$**	$S^aS^bS^e$	**28**	**$[Dy(TODGA)_3][Ni(hfacac)_3]_3$**	$S^aS^bS^e$
14	**$[Ni(TEHDGA)_2][Ni(hfacac)_3]_2$**	$S^aS^bS^e$	**29**	**$[Ni(TODGA)_2][Dy(hfacac)_4]_2$**	$S^aS^bS^e$
15	**$[Mn(TEHDGA)_2][Mn(hfacac)_3]_2$**	$S^aS^bS^e$	**30**	**$[Co(TODGA)_2][Dy(hfacac)_4]_2$**	$S^aS^bS^e$

S^a = soluble in hexane, heptane, benzene, and toluene at 10% (w/v). S^b = soluble in acetone, chloroform, dichloromethane, acetonitrile, methanol, ethanol, diethyl ether, ethyl acetate, and isopropanol at 20% (w/v). S^c = soluble in hexane, heptane, benzene, and toluene at 20% (w/v). S^d = insoluble in hexane, heptane, benzene, and toluene at 10% (w/v). S^e = insoluble in water at 0.01% (w/v).

In contrast, all lanthanide-based MILs dissolved in non-polar solvents at a concentration of 10% (w/v) MIL-to-solvent ratio regardless of the type of ligand employed. Heterogenous MIL combinations comprised of two different transition metals (MILs **25** and **26**) exhibited the same solubilities as homogenous combinations (MILs **1-3**). However, heterogenous MIL combinations incorporating both lanthanide and transition metals in the anion/cation (MILs **27-30**) possessed lower solubilities (10% w/v MIL-to-solvent ratio) in hexane, heptane, and benzene compared to 20% (w/v) for those comprised of only rare-earth metal centers (MILs **4-6**). All MILs were soluble in organic solvents, such as dichloromethane, diethyl ether, methanol, and acetone at a concentration of 20% w/v MIL-to-solvent ratio and observed to be insoluble in water even at concentrations as low as 0.01% (w/v).

3.4. Magnetic susceptibility

In contrast to conventional ILs, MILs exhibit paramagnetic properties and can respond to an external magnetic field permitting them to be easily separated from immiscible solvents using a hand-held permanent neodymium rod magnet. Unpaired electrons in the 3*d* orbitals of transition metals and 4*f* orbitals of lanthanides undergo spin alignment along the direction of the applied magnetic field and this ordering is eventually lost when the external magnet is removed. The temperature dependence of magnetization follows Curie-Weiss law which describes a linear relationship between the temperature and inverse magnetic susceptibility. The Curie-Weiss fit of the linear portion of reciprocal susceptibility plotted against temperature can reveal crucial parameters such as the effective paramagnetic moment (μ_{eff}).

Magnetic measurements for 15 MILs were carried out using a Superconducting Quantum Interference Device (SQUID) magnetometer, MPMS XL-7 (Quantum Design Inc.). The temperature dependence of magnetization for both lanthanide and transition metal-based MILs is shown in Figure 4. It was found that all MILs exhibited a linear trend for the reciprocal Susceptibility ($1/\chi$) plotted against temperature passing through origin ($T=0$, $1/\chi=0$), demonstrating paramagnetic behavior for all combinations regardless of the type of cationic ligand or metal center employed in their preparation. The Curie-Weiss plots for MILs **2**, **7**, **8**, **10**, **12**, **16**, **19**, **20**, **22**, and **24** can be found in the supporting information (Figures S1-S10). To calculate the theoretical effective magnetic moment for lanthanide-based homogenous MIL combinations, equation 1 was employed [48]:

$$\mu_{\mathrm{theor}}{}^2 = \mu_X{}^2 + \mu_X{}^2 + \mu_X{}^2 + \mu_X{}^2 \ (1)$$

According to equation 1, μ_{theor} represents the theoretical effective magnetic moment for the MIL while μ_X refers to the theoretical effective magnetic moment for each metal center. Since the lanthanide-based homogenous MIL combination contains four identical metal centers, the calculation for the theoretical effective magnetic moment could be simplified to equation 1. In the case of transition metal-based homogenous MIL combinations, the equation was modified to contain 3 μ_X terms as each MIL is comprised of 3 identical paramagnetic centers only. Table 3 provides a comparison of μ_{theor} and μ_{eff} and it was observed that the theoretical and experimentally determined values for the effective magnetic moment were found to be an exact match. The μ_{eff} ranged from 4.71 to 10.44 μ_B for transition metal-based MILs and from 14.90 to 21.08 μ_B for those comprised of lanthanides. The lowest μ_{eff} of 4.71 μ_B was obtained for the $[Ni(TODGA)_2][Ni(hfacac)_3]_2$ MIL while the highest value of 20.86 μ_B was determined for the $[Ho(TODGA)_3][Ho(hfacac)_4]_3$ MIL. It was also observed that variations in the type of cationic ligand did not alter the μ_{eff} as values of 8.03, 8.43, and 8.34 μ_B were obtained for the $[Co(TODGA)_2][Co(hfacac)_3]_2$, $[Co(TBDGA)_2][Co(hfacac)_3]_2$, and $[Co(iTBDGA)_2][Co(hfacac)_3]_2$ MILs, respectively.

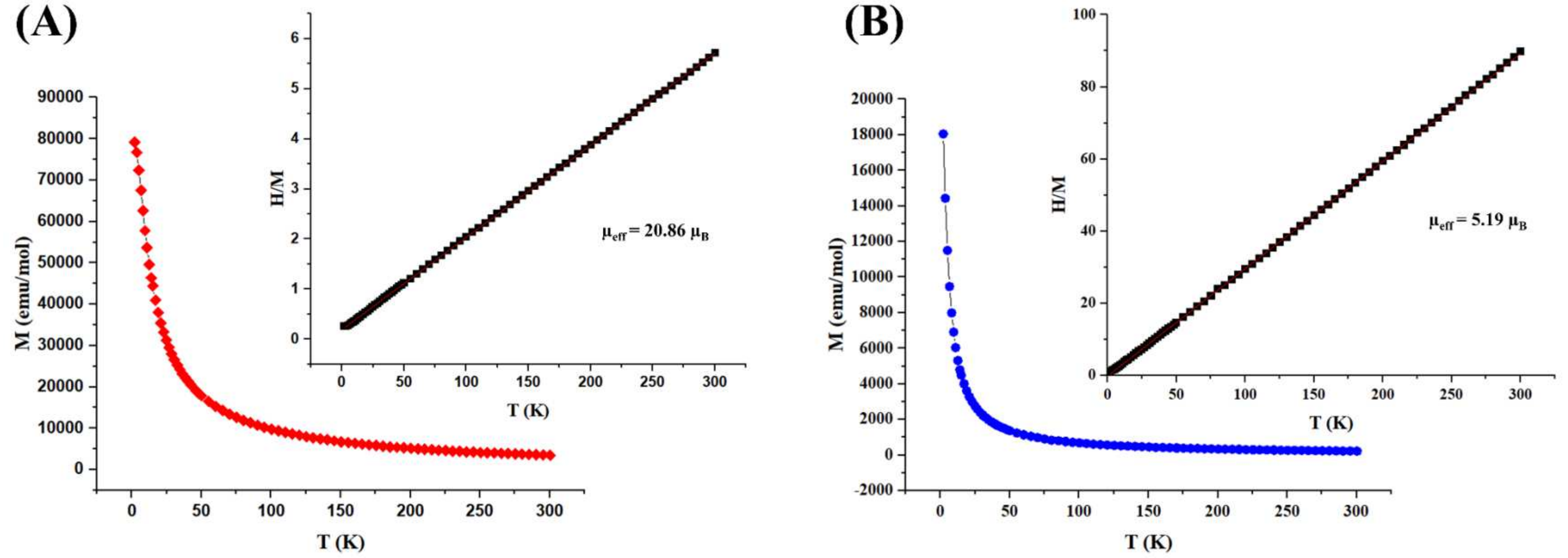


Figure 4: Magnetization of lanthanide and transition metal-based MILs as a function of temperature in an applied magnetic field of H = 20 kOe: (A) $[Ho(TODGA)_3][Ho(hfacac)_4]_3$ and (B) $[Ni(TEHDGA)_2][Ni(hfacac)_3]_2$. The inset shows the Curie-Weiss fit of the linear portion of the reciprocal susceptibility.

Therefore, the strength of magnetization of these MILs is mostly dependent on the type of metal center. Additionally, all cobalt MILs were determined to be high spin complexes. Cobalt (II), being a d^7 system, can form both low spin and high spin complexes based on the type of ligand it is interacting with. Previously, the $[P_{66614}^+][Co(hfacac)_3]_2$ MIL was determined to be a high spin complex as hexafluoroacetylacetone is a weak field ligand [29], [34]. Since μ_{eff} for cobalt MILs is in complete agreement with the μ_{theor}, all cobalt (II) metal centers in these complexes must exist in high spin states, demonstrating that the diglycolamides employed in this study are weak field ligands. A μ_{eff} of 10.44 μ_B obtained for the $[Mn(TODGA)_2][Mn(hfacac)_3]_2$ MIL was a precise match with the μ_{theor} for a high spin complex, further exemplifying diglycolamides as weak field ligands. For MIL combinations containing the same metal center in both the anion/cation, the μ_{eff} is approximately double that of those comprised of $[P_{66614}^+]$ cation and $[hfacac^-]$ metal chelates as the anion as shown in Table 3. For example, the μ_{eff} for the $[Co(TODGA)_2][Co(hfacac)_3]_2$ MIL is 8.03 μ_B compared to 4.30 μ_B for the $[P_{66614}^+][Co(hfacac)_3]_2$ MIL. In addition, magnetic properties of MILs comprised of heterogenous metal centers were investigated using MSB. Values of 6.12 and 7.02 μ_B were obtained for the $[Co(TODGA)_2][Ni(hfacac)_3]_2$ and $[Ni(TODGA)_2][Co(hfacac)_3]_2$ MILs, respectively, and were significantly different from 8.03 and 4.71 μ_B observed for the $[Co(TODGA)_2][Co(hfacac)_3]_2$ and $[Ni(TODGA)_2][Ni(hfacac)_3]_2$ MILs, demonstrating the ability to further modulate the magnetic properties while incorporating the same class of metal centers. In contrast, switching from lanthanide to transition metal centers in the anion resulted in μ_{eff} values of 13.06 and 11.98 μ_B for the $[Dy(TODGA)_3][Co(hfacac)_3]_3$ and $[Dy(TODGA)_3][Ni(hfacac)_3]_3$ MILs, respectively, compared to 20.00 μ_B obtained for the $[Dy(TODGA)_3][Dy(hfacac)_4]_3$ combination. Clearly, both the lanthanide and transition metal-based MILs can offer a much higher magnetic response than many other classes of MILs and simultaneously incorporating two different types of metal centers can result in greater variations in magnetic properties.

Table 3. Magnetic properties measured by SQUID and MSB for MILs comprised of lanthanides and transition metal centers.

MIL No.	MIL abbreviation	μ_{theor} (μ_B)	μ_{eff} (μ_B)	Reference
1	$[Co(TODGA)_2][Co(hfacac)_3]_2$	8.30	8.03	Present work
2	$[Ni(TODGA)_2][Ni(hfacac)_3]_2$	5.37	4.71	Present work
3	$[Mn(TODGA)_2][Mn(hfacac)_3]_2$	10.13	10.44[a]	Present work
4	$[Dy(TODGA)_3][Dy(hfacac)_4]_3$	21.30	20.00	Present work
5	$[Gd(TODGA)_3][Gd(hfacac)_4]_3$	15.90	14.90	Present work
6	$[Ho(TODGA)_3][Ho(hfacac)_4]_3$	21.20	20.86	Present work
7	$[Co(TBDGA)_2][Co(hfacac)_3]_2$	8.30	8.43	Present work
8	$[Ni(TBDGA)_2][Ni(hfacac)_3]_2$	5.37	5.24	Present work
10	$[Dy(TBDGA)_3][Dy(hfacac)_4]_3$	21.30	20.52	Present work
12	$[Ho(TBDGA)_3][Ho(hfacac)_4]_3$	21.20	20.63	Present work
14	$[Ni(TEHDGA)_2][Ni(hfacac)_3]_2$	5.37	5.19	Present work
16	$[Dy(TEHDGA)_3][Dy(hfacac)_4]_3$	21.30	20.52	Present work
19	$[Co(iTBDGA)_2][Co(hfacac)_3]_2$	8.30	8.34	Present work
20	$[Ni(iTBDGA)_2][Ni(hfacac)_3]_2$	5.37	4.75	Present work
22	$[Dy(iTBDGA)_3][Dy(hfacac)_4]_3$	21.30	21.08	Present work
24	$[Ho(iTBDGA)_3][Ho(hfacac)_4]_3$	21.20	20.85	Present work
25	$[Co(TODGA)_2][Ni(hfacac)_3]_2$	6.46	6.12[a]	Present work
26	$[Ni(TODGA)_2][Co(hfacac)_3]_2$	7.40	7.02[a]	Present work
27	$[Dy(TODGA)_3][Co(hfacac)_3]_3$	13.34	13.06[a]	Present work
28	$[Dy(TODGA)_3][Ni(hfacac)_3]_3$	11.79	11.98[a]	Present work
-	$[P_{66614}][Co(hfacac)_3]$	-	4.30	[29]
-	$[P_{66614}][Ni(hfacac)_3]$	-	2.80	[29]
-	$[P_{66614}][Mn(hfacac)_3]$	-	5.80	[29]

[a] Magnetic property evaluated using a magnetic susceptibility balance (MSB).

4. Conclusions

Magnetic ionic liquids constitute a class of solvents containing paramagnetic metal centers with highly tunable physico-chemical properties. While MILs are comprised of different types of ligands and metal centers, most MILs generally incorporate a single lanthanide or transition metal in either the anion or the cation. A recently developed class of MILs comprised of diglycolamide-based cationic ligands demonstrates that multiple rare-earth metals can be simultaneously incorporated into the MIL structure in order to yield combinations possessing enhanced magnetic susceptibility.

Transition metals were shown to form MILs for the first time with four different diglycolamides employed as cationic ligands. It was found that diglycolamides comprised of octyl substituents possessed enhanced thermal stability compared to those composed of butyl functional groups while branched ligands generally offered stronger metal-ligand interactions. Transition metal-based MILs exhibited higher thermal stability up to temperatures of 235 °C compared to those comprised of lanthanides while substituting rare-earth metal centers with cobalt (II) or nickel (II) in either the anion and/or cation significantly enhanced the decomposition temperature of MILs. The viscosity of MILs ranged from 9,210 to 104,390 cP at 19.9 °C with higher values obtained for combinations comprised of ligands that possessed short alkyl chain substituents. Additionally, the lowest viscosities were obtained for lanthanide metal-based MILs compared to those comprised of transition metals while values for heterogenous combinations incorporating two different types of metal centers varied between 21,410 and 29,550 cP. These hydrophobic MILs were generally soluble in most non-polar solvents including hexane, heptane, and benzene and were insoluble in water at concentrations as low as 0.01 (w/v) MIL-to-solvent ratio. It was also revealed that both lanthanide and transition metal-based MILs exhibited paramagnetic behavior and possessed enhanced magnetic susceptibility with μ_{eff} ranging from 4.71 to 20.86 μ_{B}. Despite structural variations in diglycolamides, no significant differences were observed in magnetic susceptibility when the cationic ligands were altered. In addition, all cobalt (II) metal centers formed high spin complexes thus, establishing diglycolamides as weak field ligands. This study highlights the role of diglycolamides in forming highly tunable hydrophobic MILs possessing enhanced magnetic susceptibility for both lanthanide and transition metal combinations and further demonstrates the possibility of modifying physico-chemical of these MILs by simultaneously employing two different types of metal centers within the same MIL in order to incorporate characteristics of both metals, thus establishing these MILs as highly versatile in their design and synthesis.

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Supporting Information. List of chemicals and reagents, characterization of MILs using elemental analysis, Curie-Weiss plots for select MILs, and ^{1}H and ^{13}C NMR spectra for diglycolamide-based ligands synthesized in the study.

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