Ultra-Low Viscosity and High Magnetic Susceptibility Magnetic Ionic Liquids Featuring Functionalized Diglycolic Acid Ester Rare-Earth and Transition Metal Chelates

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ABSTRACT: Magnetic ionic liquids (MILs) comprise a subcategory of ionic liquids (ILs) and contain a paramagnetic metal center allowing them to be readily manipulated by an external magnetic field. While MILs are popularly employed as solvents in catalysis, separations, and organic synthesis, most low viscosity combinations possess a hydrophilic character that limits their use in aqueous matrices. To date, no study has reported the synthesis and characterization of hydrophobic MILs with viscosities similar to those of hydrophilic MILs and organic solvents while simultaneously exhibiting enhanced magnetic and thermal properties. In this study, diglycolic acid esters are employed as ligands to chelate with paramagnetic metals to produce cations that are paired with metal chelates composed of hexafluoroacetylacetonate ligands to form MILs incorporating multiple metal centers in the cation and anion. Viscosity values below 31.6 cP were obtained for these solvents, the lowest ever reported for hydrophobic MILs. Solubilities in nonpolar solvents such as benzene were observed to be as high as 50% (w/v) MIL-to-solvent ratio while being insoluble in water at concentrations as low as 0.01% (w/v). Effective paramagnetic moment values for these solvents ranged from 5.33 to 15.56 Bohr magnetons (μ_B), with mixed metal MILs containing multiple lanthanides in the anion generally offering higher magnetic susceptibilities. MILs composed of ligands containing octyl substituents were found to possess thermal stabilities up to 190 °C. The synthetic strategies explored in this study exploit the highly tunable nature of the employed cation and anion pairs to design versatile ultra-low viscosity magnetoactive solvents that possess tremendous potential and applicability in liquid–liquid separation systems, catalysis, and microfluidics where the mechanical movement of the solvent can be easily facilitated using electromagnets.
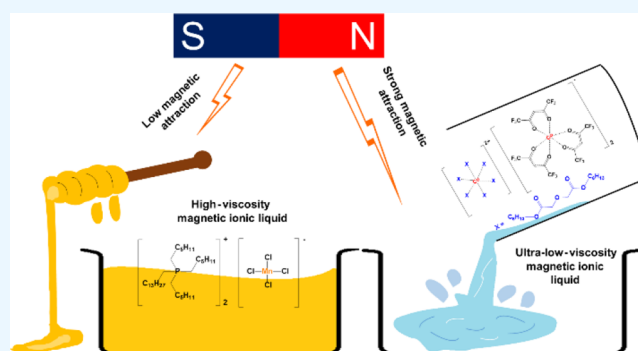
1. INTRODUCTION

Ionic liquids (ILs) are a popular choice of solvents for use in sustainable chemical research.[1,2] Their typical chemical structure consists of an organic cation paired with a weakly coordinating anion to produce ionic compounds that melt at temperatures of 100 °C or lower.[2,3] They often possess a number of customizable properties such as negligible vapor pressure,[1,4] tunable viscosity,[5] and high thermal[4,6] and chemical stability,[7] making them popular in catalysis,[8,9] organic synthesis,[1,10] and chemical separations.[11,12] Paramagnetic metal centers can be incorporated into the cation and/or anion to yield a subclass of ILs referred to as magnetic ILs (MILs).[13,14] MILs often possess similar physico-chemical properties to ILs and can additionally respond to an external magnetic field, making them easy to manipulate in many solvents using a hand-held magnet.[13,15]

Owing to advancements made in the design of their chemical structures, different classes of MILs have evolved over the years,[16,17] with key features that can influence specific MIL properties having been identified.[18,19] For example, bulky alkyl functional groups in the cation/anion can enhance the thermal stability and hydrophobicity of MILs, while employing anionic ligands containing trifluoromethyl moieties (CF$_3$) can expand their hydrophobic nature and result in reduced MIL viscosity.[13,20] Aromatic substituents in ligands have also been found to enhance the thermal stability of MILs but generally yield highly viscous solvents.[21] While their magnetic properties are primarily controlled by the type and number of paramagnetic centers, their viscosity and solvation properties (e.g., dipolar and dispersive-type interactions) can also be influenced by the metal employed.[21–23] Clearly, both the type of ligands and paramagnetic centers forming the cation/anion

can significantly influence the physical and chemical properties of MILs, which truly highlight their designer solvent nature.

Although MILs offer highly tunable physico-chemical properties, customization of their viscosities is often of significant interest in many applications.[15,24] For MILs to function as solvents, extractants, or reaction media, low viscosities are often preferred as they facilitate ease of pipetting[25] and allow rapid transport/exchange of materials.[15,26] In separation systems involving two immiscible solvents, low viscosity enables ease of MIL dispersion and subsequent phase separation without the need of tedious centrifugation and ultrasonication steps.[15,26] In addition, measuring very small quantities of MILs (e.g., microliter volumes) can be challenging due to their high viscosity, which can adversely impact accuracy, precision, and method reproducibility in applications that require high volume precision.[27,28] However, MILs generally resemble oils and possess viscosities that are two to three orders of magnitude higher than that of organic solvents.[16] The first reported MIL, 1-butyl-3-methylimidazolium tetrachloroferrate(III) ($[C_4mim^+][FeCl_4^-]$), was shown to have a viscosity of only 18 cP but is plagued by stability issues in aqueous environments.[29−31] Given hydrolysis of the $[FeCl_4^-]$ anion in water,[22] the $[MnCl_4^{2-}]$, $[CoCl_4^{2-}]$, and $[GdCl_6^{3-}]$ anions have not only demonstrated improved stability but also produced MILs with viscosities as high as 123,500 cP between 273 and 373 K.[16]

To modulate MIL viscosity, several approaches have been used to date.[16,20,32] MILs mixed with water and organic solvents have been employed to facilitate the lowering of their charge density and viscosity.[32] However, this strategy can only be applied to hydrophilic MILs. Additionally, the unique physico-chemical properties of MILs are lost when they are diluted with traditional solvents beyond a specific concentration range.[32] Generally, anions composed of hexafluoroacetylacetonate ligands $[hfacac^-]$ and bis[(trifluoromethyl)-sulfonyl]imide $[NTf_2^-]$ are employed to produce low viscosity MILs.[20,22] An unconventional approach to induce a reduction in MIL viscosity involves applying a rotational external magnetic field.[16,33] Using a supported MIL membrane (SMILM), Santos et al. reported a 21.64% increase in carbon dioxide gas permeability under the influence of an external magnetic field, which was correlated with reduced MIL viscosity and also found to be dependent on its magnetic susceptibility.[33] In a separate study, Daniel and co-workers observed a 51% increase in α-pinene permeability in dodecane through a SMILM composed of the $[C_4mim^+][FeCl_4^-]$ MIL. While a 10.3% reduction in MIL viscosity was obtained using a 2.0 Tesla (T) magnet, the enhanced membrane permeability was also attributed to an increase in analyte solubility at the elevated magnetic field.[34]

In an attempt to design a highly customizable class of MILs, considerable effort has been made to incorporate specific functional groups and structural features that can impart reduced viscosity and enhanced magnetic susceptibility.[35] A new class of MILs composed of $[hfacac^-]$ metal chelates was recently reported that simultaneously incorporate multiple lanthanide and transition metal centers in both the cation and anion.[36,37] Compared to all other previously reported classes, these MILs possess tremendous structural tunability potential and involve combinations that simultaneously incorporate polar functional groups and two different types of paramagnetic centers in the cation/anion.[37] While these MILs offer

enhanced hydrophobicity, thermal stability, and effective magnetic moments (μ_{eff}) of up to 21.08 Bohr magnetons (μ_B), they suffer from significantly high viscosity with values ranging from 9210 to 104,390 cP at 19.9 °C.[36,37] Moreover, aromatic moieties that can impart specific $\pi-\pi$ interactions and confer additional chemical and thermal stability[21] could not be incorporated in the MIL chemical structure as they add steric bulk and result in increased viscosity. Given that $[hfacac^-]$ metal chelates employed as anions can yield lower viscosities, the cationic component of these MILs remains a key target for further chemical structure modification. To date, only diglycolamides (DGAs) have been used as cationic ligands in these MILs, and no other multidentate chelating species have been explored to lower their viscosity.

In this study, digylcolic acid esters (DGEs) were employed as cationic ligands in the synthesis of fifteen (15) MILs composed of multiple paramagnetic centers. Their physico-chemical properties were thoroughly characterized and benchmarked against previous classes of MILs. Ultra-low viscosities below 31 cP were obtained for these MILs, comparable to that of organic solvents such as 1-octanol (7.59 cP at 25 °C). Cationic ligands incorporating both aromatic and aliphatic alkyl substituents were employed to prepare MILs that simultaneously contain two different types of metal centers in their chemical structure, resulting in effective magnetic moments (μ_{eff}) as high as 15.56 Bohr magnetons (μ_B). Varying the length of alkyl moieties or the incorporation of cyclic functional groups in the cationic ligands was found to influence MIL thermal stability, with those composed of octyl substituents being stable at temperatures up to 190 °C. The new generation of MILs excel at offering ideal physico-chemical properties often sought out in designer solvents. This study explores the distinct design of DGE-based MILs and demonstrates that such combinations produce compounds that are less viscous compared to many organic solvents, making them highly appealing in catalysis, organic synthesis, as well as chemical and electrochemical separations as a sustainable replacement for traditional solvents, where their paramagnetic properties can be readily exploited.

2. EXPERIMENTAL SECTION

2.1. Instrumentation and Equipment. Nuclear magnetic resonance (NMR) spectroscopy was conducted using Bruker 400 and 600 MHz spectrometers. Elemental analysis was performed using a Thermo Scientific FlashSmart 2000 CHNS/O Combustion Elemental Analyzer (Waltham, MA, USA). A Brookfield DV1 cone and plate viscometer equipped with a CPA-51Z cone spindle was employed to obtain viscosity measurements at 21.6 °C using approximately 0.5 g of each MIL after extensive drying for 48 h under vacuum. Magnetic properties were analyzed using a magnetic susceptibility balance (MSB, Sherwood Scientific, Cambridge, UK) and a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS XL-7). The thermal stability of MILs was measured from 40 to 350 °C at a ramp rate of 5 °C min^{-1} by performing thermogravimetric analysis (TGA) using a NETZSCH STA 449 F1 Jupiter thermal analyzer (Selb, Germany). Additionally, gas chromatography (GC) was also used by employing a previously reported method and temperature program with a lower ramp rate of 1 °C min^{-1}[21,37] in order to investigate the MIL stability at elevated temperatures with greater sensitivity and precision. All measurements were performed on an Agilent Technologies
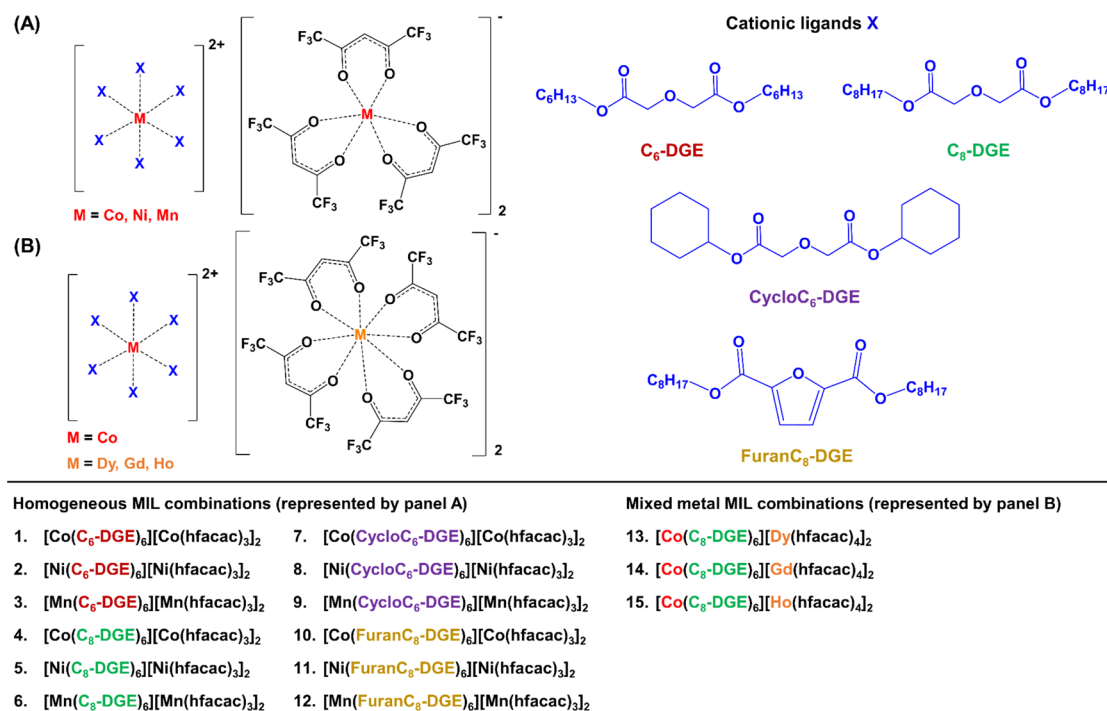
Figure 1. Numbering scheme and chemical structures used for MILs examined in this study. Abbreviations: dihexyl-2,2′-oxidiacetate (C$_6$-DGE), dioctyl-2,2′-oxidiacetate (C$_8$-DGE), dicyclohexyl-2,2′-oxidiacetate (CycloC$_6$-DGE), dioctylfuran-2,5-dicarboxylate (FuranC$_8$-DGE), and hexafluoroacetylacetonate ligands ([hfacac$^-$]). (A) Chemical structure of MILs containing transition metals in the cation and anion and (B) chemical structure of MILs composed of transition and rare-earth metals in the cation and anion, respectively.

7890B gas chromatograph (Santa Clara, CA, USA) equipped with a flame ionization detector (FID).

2.2. Preparation and Characterization of Cationic Ligands.

A detailed list of reagents/starting materials used to prepare the MILs, their purities, and vendor information is provided in the Supporting Information. All DGE ligands were synthesized using a slightly modified version of a previously reported reaction scheme,[38] and their chemical structures are provided in Figure 1. A mixture of triethylamine (90 mmol) and 40 mmol alcohol (1-hexanol, 1-octanol, or cyclohexanol) was placed in a 250 mL round bottom flask (RBF) and dissolved in 100 mL of dichloromethane. Diglycolyl chloride (2,2′-oxydiacetyl chloride, 20 mmol) was added dropwise to the contents of the flask and stirred for 6 h at room temperature and pressure. The resulting solution was transferred to a 250 mL separatory funnel and washed six times with 30 mL of 10% HCl solution followed by a final wash with 50 mL of 5% (w/w) NaHCO$_3$ solution. Dichloromethane was removed under reduced pressure, and the products were dissolved in 50 mL of hexane and filtered under gravity to remove any remaining salt impurities.

To prepare a DGE ligand containing an aromatic substituent (see cationic ligands in Figure 1), 2,5-furandicarboxylic acid (20 mmol) was transferred into a 250 mL RBF along with an excess (200 mmol) of thionyl chloride (SOCl$_2$). Five drops of N,N-dimethylformamide (N,N-DMF) were added to the flask, and its contents were then refluxed at 50 °C for 24 h until a homogeneous clear solution was obtained.[39] Excess SOCl$_2$ was removed under reduced pressure using a rotary evaporator, and the resulting furan-2,5-dicarbonyl dichloride was reacted with 1-octanol using the same procedure outlined for diglycolyl chloride. The following DGE ligands were prepared and characterized using ^{13}C and ^{1}H NMR (spectra are provided in the Supporting Information):

2.2.1. NMR Analysis of Dihexyl-2,2′-oxidiacetate (C$_6$-DGE).
Pale yellow liquid. Yield of 97%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.25 (s, 1H), 4.18 (t, J = 6.8 Hz, 1H), 1.66 (p, J = 6.9 Hz, 1H), 1.40−1.26 (m, 3H), 0.91 (t, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 169.79, 68.65, 68.08, 65.55, 65.12, 31.33, 28.46, 28.42, 25.45, 22.45, 13.91.

2.2.2. NMR Analysis of Dioctyl-2,2′-oxidiacetate (C$_8$-DGE).
Pale yellow liquid. Yield of 98%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.23 (s, 4H), 4.15 (t, J = 6.8 Hz, 4H), 1.68−1.61 (m, 4H), 1.36−1.22 (m, 20H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 169.82, 68.11, 65.16, 31.74, 29.14, 29.12, 28.52, 28.47, 25.80, 25.77, 22.60, 14.04.

2.2.3. NMR Analysis of Dicyclohexyl-2,2′-oxidiacetate (CycloC$_6$-DGE).
Yellow liquid. Yield of 97%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.86 (ddp, J = 13.4, 8.5, 4.6 Hz, 2H), 4.21 (s, 4H), 1.90−1.84 (m, 4H), 1.76−1.70 (m, 4H), 1.59−1.50 (m, 3H), 1.48−1.33 (m, 9H), 1.28−1.23 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 169.26, 73.57, 73.19, 68.32, 33.45, 33.38, 31.55, 31.50, 25.26, 25.14, 23.79, 23.68.

2.2.4. NMR Analysis of Dioctylfuran-2,5-dicarboxylate (FuranC$_8$-DGE).
Dark yellow liquid that turns into an amorphous solid over time. Yield of 95%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.60−7.48 (m, 1H), 7.29 (d, J = 7.4 Hz, 1H), 4.37 (t, J = 6.8 Hz, 1H), 3.99 (ddt, J = 55.3, 10.1, 6.6 Hz, 3H), 1.74 (dp, J = 56.3, 6.9 Hz, 4H), 1.46−1.23 (m, 21H), 0.90 (t, J = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 157.61, 155.84, 155.67, 149.59, 147.34, 123.87, 123.20, 118.45, 66.27, 62.33, 31.76, 29.52, 29.15, 29.14, 29.12, 28.52, 25.81, 25.77, 22.63, 14.07.

2.3. Synthesis and Characterization of MILs.
All MILs examined in this study were prepared using a modified version of a previously reported reaction route.[37] Ammonium-based anion salts composed of [hfacac$^-$] metal chelates were synthesized using a widely reported reaction mechanism.[21,22]

Using a one-pot synthesis approach, DGE ligands (5 mmol) were solubilized in 60 mL of methanol and reacted over 24 h with 2.5 mmol transition metal chlorides ($NiCl_2$, $CoCl_2$, and $MnCl_2.4H_2O$) in a 2:1 molar ratio to form chloride-based salts of the cation system. The resulting cationic salt was mixed with 5 mmol [hfacac$^-$] metal chelates composed of transition metal centers at a 1:2 molar ratio. Methanol was removed under reduced pressure, and the contents of the flask were solubilized in 100 mL of diethyl ether and filtered under gravity to remove solid byproducts. The filtrate was transferred to a 250 mL separatory funnel and repeatedly washed with 10 mL of water until the aqueous layer produced no precipitate through an anion-exchange mechanism with $AgNO_3$. The solvent was evaporated under reduced pressure, and the MIL was dissolved in 60 mL of hexane. Any solid byproducts and/or excess ammonium-based anion salts were removed by filtering under gravity, and hexane was subsequently removed using rotary evaporation. The final MIL was dried under vacuum for 48 h prior to further characterization. Homogeneous MIL combinations composed of the same transition metals in both the cation/anion using different DGE ligands were synthesized, as shown in Figure 1 (MIL **1** to **12**).

To prepare mixed metal MIL combinations, the cobalt-containing cation salts were mixed with 5 mmol [hfacac$^-$] metal chelates of lanthanides (Dy, Gd, Ho) in the same molar ratio (1:2), and the purification steps were performed in a manner identical to that of transition metal MILs. Lanthanide-containing MILs were prepared as MILs composed of two different types of metal centers, as indicated in Figure 1 (MIL **13** to **15**). The purities of all MILs were characterized using CHN elemental analysis.

2.3.1. MIL Characterization. **MIL 1**: Dark red, nonviscous liquid. Elemental analysis calculated (%) for $Co_3C_{126}H_{186}F_{36}O_{42}$: C, 46.80; H, 5.80; N, 0.00. Found: C, 46.33; H, 5.98; N, 0.14.

MIL 2: Dark green, nonviscous liquid. Elemental analysis calculated (%) for $Ni_3C_{126}H_{186}F_{36}O_{42}$: C, 46.81; H, 5.80; N, 0.00. Found: C, 46.88; H, 6.38; N, 0.41.

MIL 3: Dark yellow, nonviscous liquid. Elemental analysis calculated (%) for $Mn_3C_{126}H_{186}F_{36}O_{42}$: C, 46.98; H, 5.82; N, 0.00. Found: C, 46.96; H, 5.26; N, 0.04.

MIL 4: Bright red, nonviscous liquid. Elemental analysis calculated (%) for $Co_3C_{150}H_{234}F_{36}O_{42}$: C, 50.46; H, 6.61; N, 0.00. Found: C, 51.12; H, 6.33; N, 0.57.

MIL 5: Bright green, nonviscous liquid. Elemental analysis calculated (%) for $Ni_3C_{150}H_{234}F_{36}O_{42}$: C, 50.47; H, 6.61; N, 0.00. Found: C, 50.48; H, 7.41; N, 0.50.

MIL 6: Bright yellow, nonviscous liquid. Elemental analysis calculated (%) for $Mn_3C_{150}H_{234}F_{36}O_{42}$: C, 50.63; H, 6.63; N, 0.00. Found: C, 50.13; H, 7.02; N, 0.15.

MIL 7: Red, nonviscous liquid. Elemental analysis calculated (%) for $Co_3C_{126}H_{162}F_{36}O_{42}$: C, 47.16; H, 5.09; N, 0.00. Found: C, 45.27; H, 5.49; N, 0.200.

MIL 8: Green, nonviscous liquid. Elemental analysis calculated (%) for $Ni_3C_{126}H_{162}F_{36}O_{42}$: C, 47.17; H, 5.09; N, 0.00. Found: C, 47.11; H, 5.83; N, 0.14.

MIL 9: Yellow, nonviscous liquid. Elemental analysis calculated (%) for $Mn_3C_{126}H_{162}F_{36}O_{42}$: C, 47.33; H, 5.11; N, 0.00. Found: C, 47.91; H, 5.98; N, 0.13.

MIL 10: Bright red, nonviscous liquid that becomes semisolid over time. Elemental analysis calculated (%) for $Co_3C_{162}H_{222}F_{36}O_{42}$: C, 52.56; H, 6.04; N, 0.00. Found: C, 52.70; H, 7.42; N, 0.24.

MIL 11: Bright green, nonviscous liquid that becomes semisolid over time. Elemental analysis calculated (%) for $Ni_3C_{162}H_{222}F_{36}O_{42}$: C, 52.57; H, 6.05; N, 00. Found: 52.78; H, 7.52; N, 0.50.

MIL 12: Bright yellow, nonviscous liquid that becomes semisolid over time. Elemental analysis calculated (%) for $Mn_3C_{162}H_{222}F_{36}O_{42}$: C, 52.73; H, 6.06; N, 0.00. Found: C, 49.03; H, 6.25; N, 0.23.

MIL 13: Pale red, nonviscous liquid. Elemental analysis calculated (%) for $CoDy_2C_{160}H_{244}F_{48}O_{46}$: C, 45.76; H, 5.86; N, 0.00. Found: C, 47.84; H, 5.83; N, 0.19.

MIL 14: Pale red, nonviscous liquid. Elemental analysis calculated (%) for $CoGd_2C_{160}H_{244}F_{48}O_{46}$: C, 45.88; H, 5.87; N, 0.00. Found: C, 44.81; H, 5.99; N, 0.19.

MIL 15: Pale red, nonviscous liquid. Elemental analysis calculated (%) for $CoHo_2C_{160}H_{244}F_{48}O_{46}$: C, 45.71; H, 5.85; N, 0.00. Found: C, 45.12; H, 4.78; N, 0.17.

3. RESULTS AND DISCUSSION

3.1. Designing Highly Tunable Cation and Anion Pairs to Produce Low Viscosity Hydrophobic MILs. MILs can be categorized as either radical-based or paramagnetic metal-containing solvents.[17] Solvents composed of metal centers can be further classified as metal anion-based MILs (type A) and those formed by a metal cation (type B).[17,37] Although roughly 88% of applications requiring enhanced precision and method reproducibility popularly employ type A MILs,[17] those solvents composed of [hfacac$^-$] metal chelates have been increasingly favored over other anions as they result in enhanced chemical/thermal stabilities and reasonably low viscosities (below 276.6 cP at 23.7 °C).[21,22] In an effort to produce ultra-low viscosity MILs with high magnetic susceptibility, it was vital that [hfacac$^-$]-based anions be paired with suitable cations that permit the incorporation of multiple paramagnetic metals in the MIL chemical structure. While employing dicationic and tricationic cations have previously resulted in the formation of MILs possessing 2−3 [$FeCl_3Br^-$] anions, their synthesis is complex, and some combinations often produce highly viscous MILs.[13] One possible approach is to pair [hfacac$^-$] metal chelates with cations formed by *N*-alkylimidazole ligands coordinated to transition metal centers,[20] but these monodentate ligands often interact less strongly with paramagnetic metals compared to multidentate ligands.[40] Employing DGA ligands to produce coordinated cationic species and using them to form MILs with [hfacac$^-$]-based anions[36,37] were an attempt to combine desirable features of both A and B types of MILs;[17] therefore, this cation/anion system was a practical choice to drastically lower their viscosities in order to make them accessible to a wider range of scientific applications.

Given that long alkyl chain moieties can significantly enhance MIL viscosity, emphasis was placed on eliminating bulky alkyl substituents as part of ligand design. Since tertiary amides were the basis of previously employed DGA ligands,[36,37] they possessed multiple bulky alkyl chains that imparted a significant hydrophobic character. To maintain MIL hydrophobicity and design cationic ligands with shorter alkyl functional groups, primary alcohols were chosen to react with diglycolyl chloride, resulting in a smaller number of alkyl moieties within the cationic ligands compared to that with the DGA ligands. To explore the effect of varying the length of alkyl substituents on the physico-chemical properties of MILs, both hexyl- and octyl-based ester ligands (C_6-DGE and C_8-

Table 1. Viscosity Data Obtained at 21.7 °C and Magnetic Properties Measured by SQUID and MSB for MILs Composed of Rare-Earth and Transition Metals

MIL No.	MIL abbreviation	Viscosity (cP)	μ_{theor} (μ_B)	μ_{eff} (μ_B)[a]	Reference
1	$[Co(C_6\text{-}DGE)_6][Co(hfacac)_3]_2$	175.0	8.30	8.11	Present work
2	$[Ni(C_6\text{-}DGE)_6][Ni(hfacac)_3]_2$	248.6	5.37	5.48	Present work
3	$[Mn(C_6\text{-}DGE)_6][Mn(hfacac)_3]_2$	63.2	10.13	10.42	Present work
4	$[Co(C_8\text{-}DGE)_6][Co(hfacac)_3]_2$	31.6	8.30	8.57	Present work
5	$[Ni(C_8\text{-}DGE)_6][Ni(hfacac)_3]_2$	119.1	5.37	5.33	Present work
6	$[Mn(C_8\text{-}DGE)_6][Mn(hfacac)_3]_2$	96.3	10.13	10.25	Present work
7	$[Co(CycloC_6\text{-}DGE)_6][Co(hfacac)_3]_2$	639.4	8.30	8.11	Present work
8	$[Ni(CycloC_6\text{-}DGE)_6][Ni(hfacac)_3]_2$	827.6	5.37	5.53	Present work
9	$[Mn(CycloC_6\text{-}DGE)_6][Mn(hfacac)_3]_2$	478.9	10.13	9.96	Present work
10	$[Co(FuranC_8\text{-}DGE)_6][Co(hfacac)_3]_2$	354.7[b]	8.30	8.27	Present work
11	$[Ni(FuranC_8\text{-}DGE)_6][Ni(hfacac)_3]_2$	453.5[b]	5.37	5.51	Present work
12	$[Mn(FuranC_8\text{-}DGE)_6][Mn(hfacac)_3]_2$	291.8[b]	10.13	10.04	Present work
13	$[Co(C_8\text{-}DGE)_6][Dy(hfacac)_4]_2$	137.2	15.56	15.38	Present work
14	$[Co(C_8\text{-}DGE)_6][Gd(hfacac)_4]_2$	149.1	12.17	12.43	Present work
15	$[Co(C_8\text{-}DGE)_6][Ho(hfacac)_4]_2$	216.4	15.63	15.56	Present work
-	$[P_{66614}][Co(hfacac)_3]$	575.8[c]	4.75	4.30[f]	(22)
-	$[P_{66614}][Ni(hfacac)_3]$	927.9[c]	3.10	2.80[f]	(22)
-	$[P_{66614}][Mn(hfacac)_3]$	401.8[c]	5.85	5.80[f]	(22)
-	$[P_{66614}]_3[GdCl_6]$	28,230[d]	7.95	7.86[f]	(16)
-	$[P_{66614}]_2[CoCl_4]$	123,500[d]	4.75	4.45[f]	(16)
-	$[P_{66614}]_2[MnCl_4]$	112,300[d]	5.85	5.81[f]	(16)
-	$[Co(TODGA)_2][Co(hfacac)_3]_2$	28,310[e]	8.30	8.03[f]	(36)
-	$[Ni(TODGA)_2][Ni(hfacac)_3]_2$	33,830[e]	5.37	4.71[f]	(36)
-	$[Dy(TODGA)_3][Dy(hfacac)_4]_3$	9,210[e]	21.30	20.00[f]	(36)
-	$[Gd(TODGA)_3][Gd(hfacac)_4]_3$	13,640[e]	15.90	14.90[f]	(36)
-	$[Ho(TODGA)_3][Ho(hfacac)_4]_3$	10,530[e]	21.20	20.86[f]	(36)

[a]Effective magnetic moment calculated using magnetic susceptibility measurements performed on a magnetic susceptibility balance. [b]MIL turns into an amorphous solid when left to stand overnight. [c]Viscosity measurement reported at 23.7 °C. [d]Viscosity measurement reported at 20.0 °C. [e]Viscosity measurement reported at 19.9 °C. [f]Effective magnetic moment calculated using magnetic susceptibility measurements performed on a SQUID magnetometer.

DGE in Figure 1) were tested. Additionally, 1-hexanol and cyclohexanol were chosen as starting materials to synthesize DGE to examine differences that may arise from using structural isomers of ligands. In an attempt to embed aromatic functional groups in the ligands, 2,5-furandicarboxylic acid was chosen to synthesize FuranC₈-DGE as it permitted the incorporation of a single conjugated ring structure without imparting excess bulk to the DGE ligand.

3.2. Optimizing the General Synthetic Scheme for Lanthanide and Transition Metal MILs. To optimize the synthetic route, it was important to determine the number of DGE ligands required to form a single cation unit. Given that transition metals were previously found to chelate with DGA ligands in a 1:2 stoichiometry to form the cation,[37] the same molar ratio was employed between metal chlorides and DGE ligands. As all reagents and intermediates were completely soluble in methanol, a one-pot synthesis method was preferred to prepare the chloride-based cationic salt followed by an anion-exchange reaction with the ammonium-based [hfacac⁻] metal salts of both lanthanides and transition metals in a 1:2 molar ratio to produce the final MIL. However, CHN

elemental analysis (see Section 2.3) revealed that the transition metal center was coordinated to 6 DGE ligands (Figure 1), unlike 2 DGA ligands observed in a previous study,[37] which can be attributed to less steric bulk. Additionally, only three hexafluoroacetylacetonate ligands were chelated to the transition metals (Figure 1A) compared to lanthanides (Figure 1B), which is consistent with other studies.[22,37] Based on the aforementioned molar ratios, DGE ligands were identified as the limiting reagent, and hence, excess metal chloride used in the synthesis of the cation system was removed by the aqueous layer during the washing step. Excess ammonium-based [hfacac⁻] metal salts were also removed during the final wash with hexane, and the recovered materials were dried and reused. It was important to maintain an excess of the [hfacac⁻] metal chelate salts as many reagents and intermediate products were sufficiently hydrophobic to be extracted into diethyl ether during purification. However, only the final MIL was soluble in hexane, and any excess reagent/intermediate was removed as a precipitate.

3.3. Effect of Cationic Ligands and Metal Centers of DGE-Based MILs on Viscosity. The viscosity of solvents can
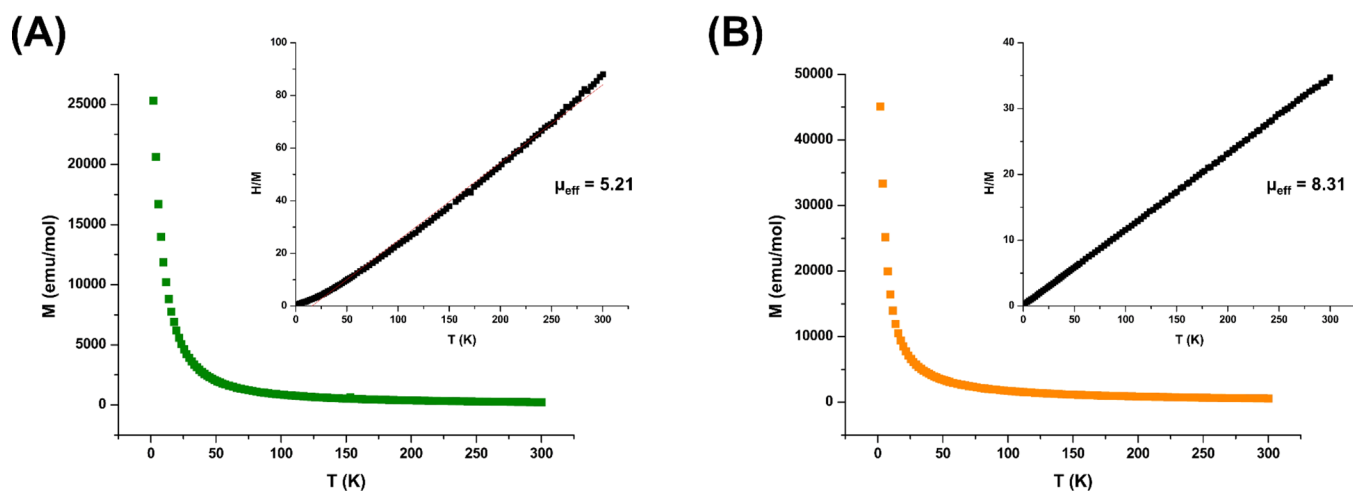
Figure 2. Magnetization of Ni- and Mn-based MILs studied as a function of temperature under an applied magnetic field of H = 20 kOe: (A) $[Ni(C_6\text{-}DGE)_6][Ni(hfacac)_3]_2$ and (B) $[Mn(C_6\text{-}DGE)_6][Mn(hfacac)_3]_2$. The inset shows the Curie−Weiss fit of the linear portion of the reciprocal susceptibility.

strongly influence their selection in many applications.[41,42] For instance, the conductivity of ILs has been reported to be inversely proportional to their viscosity,[41,43] thereby limiting the movement of ions/charges in electrochemical applications. In microreactors, highly viscous ILs often result in lower mass transfer coefficients,[42] which can lead to suboptimal extraction efficiencies of products/analytes and enhanced energy costs. Given that MILs generally possess similar chemical structures to ILs, they are predicted to behave in a similar fashion when exhibiting higher viscosity. To date, the viscosities of MILs have been reported to range from 18 to 100,000 cP at 25 °C,[16,30] but the less viscous combinations have always exhibited a hydrophilic character with very little use in applications involving aqueous matrices where it is desired that the MIL maintains a separate phase.

Viscosity measurements were conducted at 21.7 °C for 15 lanthanide and transition metal MILs examined in this study. As shown in Table 1, it was found that all MILs exhibited viscosities lower than 827.6 cP under ambient conditions with the lowest value of 31.6 cP obtained for the $[Co(C_8\text{-}DGE)_6][Co(hfacac)_3]_2$ MIL. Compared to the $[Co(C_6\text{-}DGE)_6][Co(hfacac)_3]_2$ MIL (175.0 cP), a significantly higher value of 639.4 cP was observed for the $[Co(CycloC_6\text{-}DGE)_6][Co(hfacac)_3]_2$ MIL, demonstrating that MILs composed of cyclic alkyl substituents offer stronger intermolecular forces. Similar observations were made for Ni- and Mn-based MILs composed of the same ligands by comparing MILs **2** and **3** with MILs **8** and **9**, further exemplifying that structural isomers of cationic ligands can significantly influence MIL viscosity. The lowest viscosities were generally observed for solvents composed of the $C_8\text{-}DGE$ ligand compared to those composed of the $C_6\text{-}DGE$ ligand incorporating shorter alkyl chains, as consistent with previously studied MILs prepared using DGA ligands. Consequently, the viscosity values of 31.6, 119.1, and 96.3 cP were obtained for the Co, Ni, and Mn MILs (MILs **4** to **6**), respectively. However, as previously observed for other classes of MILs,[21] installing aromatic moieties in the cationic ligands (FuranC_8-DGE) produced a moderately high viscosity Co MIL (354.7 cP) compared to MIL **6** prepared using the $C_8\text{-}DGE$ ligand with identical metal centers in the cation/anion.

The steric bulk of the cation was found to be an important factor in modulating MIL viscosity. Since viscosity can be influenced by metal−ligand bond distances, the impact of varying the type of metal center was investigated. In general, the highest viscosity solvent using any DGE ligand was obtained for Ni-based MILs compared to those composed of Co and Mn metal centers, which can be attributed to the smaller atomic radius of nickel, leading to a compact cation and stronger intermolecular forces.[22,37] Despite forming larger anions, incorporating lanthanides in mixed metal combinations (MILs **13** to **15**) did not dramatically lower the MIL viscosity compared to those composed of transition metals in both the cation and anion. Irrespective of the type of metal center, the size of the cation coordinated to the DGE ligands is perceived to be larger than that of the DGA ligands due to a larger number of cationic ligands chelated to the metal. Additionally, the individual viscosities of neat DGE ligands were observed to be significantly lower compared to previously employed DGA ligands.[37] Consequently, the viscosities of the $[Co(C_6\text{-}DGE)_6][Co(hfacac)_3]_2$ and $[Ni(C_6\text{-}DGE)_6][Ni(hfacac)_3]_2$ MILs were only 175.0 and 248.6 cP at 21.7 °C (Table 1), respectively, compared to the previously reported $[Co(TODGA)_2][Co(hfacac)_3]_2$ (28,310 cP) and $[Ni(TODGA)_2][Ni(hfacac)_3]_2$ (33,830 cP) MILs at 19.9 °C.[37] Images showing the ability of phosphonium, TODGA, and DGE-based MILs to flow under gravity are provided in the Supporting Information (Figures S1−S3).

3.4. Magnetic Properties of Transition-Based and Mixed Metal MILs. In contrast to ILs and traditional organic solvents, MILs actively respond to a hand-held magnet, allowing them to be easily manipulated in other nonmiscible solvents. Paramagnetic transition metals and lanthanides possess unpaired electrons in their 3*d* and 4*f* orbitals, respectively, that undergo temporary spin alignment under an external magnetic field. This ordering is eventually lost upon removing the magnetic field, leaving the MILs demagnetized. A linear relationship exists between the inverse of magnetic susceptibility of paramagnetic materials and temperature, in accordance with the Curie−Weiss law. The linear region of the reciprocal susceptibility plotted as a function of temperature (Curie−Weiss fit) can be used to obtain the effective

Table 2. Decomposition/Degradation Temperatures and Solubility of Lanthanide and Transition Metal-Based MILs Determined in 14 Different Solvents at three Different Concentrations

MIL No.	MIL abbreviation	Solubility	Onset of MIL volatilization (°C)[1]	Onset of MIL volatilization (°C)[2]	Reference
1	[Co(C$_6$-DGE)$_6$][Co(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^e S^f	168	255.3	Present work
2	[Ni(C$_6$-DGE)$_6$][Ni(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^e S^f	166	257.0	Present work
3	[Mn(C$_6$-DGE)$_6$][Mn(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^e S^f	168	256.8	Present work
4	[Co(C$_8$-DGE)$_6$][Co(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^f	185	262.9	Present work
5	[Ni(C$_8$-DGE)$_6$][Ni(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^f	190	264.4	Present work
6	[Mn(C$_8$-DGE)$_6$][Mn(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^f	182	259.1	Present work
7	[Co(CycloC$_6$-DGE)$_6$][Co(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^e S^f	133	200.1	Present work
8	[Ni(CycloC$_6$-DGE)$_6$][Ni(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^e S^f	154	182.2	Present work
9	[Mn(CycloC$_6$-DGE)$_6$][Mn(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^e S^f	159	176.9	Present work
10	[Co(FuranC$_8$-DGE)$_6$][Co(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^f	147	163.0	Present work
11	[Ni(FuranC$_8$-DGE)$_6$][Ni(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^f	142	160.6	Present work
12	[Mn(FuranC$_8$-DGE)$_6$][Mn(hfacac)$_3$]$_2$	S^a S^b S^c S^d S^f	144	160.4	Present work
13	[Co(C$_8$-DGE)$_6$][Dy(hfacac)$_4$]$_2$	S^a S^b S^c S^d S^f	131	182.3	Present work
14	[Co(C$_8$-DGE)$_6$][Gd(hfacac)$_4$]$_2$	S^a S^b S^c S^d S^f	126	172.9	Present work
15	[Co(C$_8$-DGE)$_6$][Ho(hfacac)$_4$]$_2$	S^a S^b S^c S^d S^f	115	183.3	Present work
-	[P$_{66614}$][Co(hfacac)$_3$]	S^a S^b S^f	130	-^{g}	(22)
-	[P$_{66614}$][Ni(hfacac)$_3$]	S^a S^b S^f	225	-^{g}	(22)
-	[P$_{66614}$][Mn(hfacac)$_3$]	S^a S^b S^f	155	-^{g}	(22)
-	[Co(TODGA)$_2$][Co(hfacac)$_3$]$_2$	S^a S^b S^f	231	-^{g}	(36)
-	[Ni(TODGA)$_2$][Ni(hfacac)$_3$]$_2$	S^a S^b S^f	235	-^{g}	(36)
-	[Dy(TODGA)$_3$][Dy(hfacac)$_4$]$_3$	S^a S^b S^c S^f	175	-^{g}	(36)
-	[Gd(TODGA)$_3$][Gd(hfacac)$_4$]$_3$	S^a S^b S^c S^f	183	-^{g}	(36)
-	[Ho(TODGA)$_3$][Ho(hfacac)$_4$]$_3$	S^a S^b S^c S^f	192	-^{g}	(36)

[1]MIL degradation temperature measured using the GC-FID approach. The onset of MIL volatilization/degradation was determined by monitoring an exponential increase in response beyond a value of 2000 pA of the detector. [2]MIL degradation temperature measured using TGA at 10% weight loss. 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, soluble in acetone, chloroform, dichloromethane, methanol, ethanol, diethyl ether, ethyl acetate, isopropanol hexane, heptane, benzene, and toluene at 50% (w/v); S^e, insoluble in acetonitrile at 50% (w/v); S^f, insoluble in water at 0.01% (w/v). ^{g}MIL characterization not reported using TGA.

paramagnetic moment (μ_{eff}), which is a temperature-independent measure of magnetic properties.

In total, 15 MILs incorporating rare-earth and transition metals were examined using a MSB, and equations used to obtain data are presented in the Supporting Information. Table 1 provides the μ_{eff} values (in μ_B/formula unit) for all MILs analyzed using MSB. The experimentally determined μ_{eff} values for the MILs were found to range from 5.33 to 15.56 μ_B per formula unit, which matches quite well with corresponding theoretically calculated values. Compared to a value of 5.48 μ_B for the [Ni(C$_6$-DGE)$_6$][Ni(hfacac)$_3$]$_2$ MIL, the μ_{eff} was approximately double for the [Mn(C$_6$-DGE)$_6$][Mn(hfacac)$_3$]$_2$ MIL (10.42 μ_B) as each Mn metal center offers higher paramagnetic moment ($\sim$5.87 μ_B; almost twice) compared to Ni ($\sim$3.15 μ_B). Varying the cationic ligand did not alter the μ_{eff} as values of 8.57, 8.11, and 8.27 μ_B were obtained for the [Co(C$_8$-DGE)$_6$][Co(hfacac)$_3$]$_2$, [Co(CycloC$_6$-DGE)$_6$][Co-(hfacac)$_3$]$_2$, and [Co(FuranC$_8$-DGE)$_6$][Co(hfacac)$_3$]$_2$ MILs, respectively, demonstrating that magnetic susceptibility is primarily dependent on the type of paramagnetic metal center. Higher μ_{eff} values were observed for the [Co(C$_8$-DGE)$_6$][Gd-(hfacac)$_4$]$_2$ (12.43 μ_B) and [Co(C$_8$-DGE)$_6$][Ho(hfacac)$_4$]$_2$

(15.56 μ_B) mixed metal MILs due to the presence of multiple lanthanides in the anion. Irrespective of the type of cationic ligands, all Mn and Co MILs formed high-spin complexes, given the precise match between the μ_{theo} and μ_{eff} values calculated for high-spin states. Additionally, the μ_{eff} for DGE-based MILs was found to be comparable to those formed using DGA ligands (Table 1) and approximately double that of those composed of phosphonium cations.

The magnetic properties of transition metal MILs were further studied using a SQUID magnetometer to confirm their paramagnetic nature as well as if any magnetic transition occurs in the samples. Figure 2 demonstrates the magnetization of Ni- and Mn-based MILs plotted as a function of temperature. All MILs exhibited a linear trend for the reciprocal susceptibility ($1/\chi$) vs temperature passing through origin ($T = 0$, $1/\chi = 0$), demonstrating paramagnetic behavior irrespective of the type of metal or ligand used. The calculated μ_{eff} of 5.21 μ_B for the [Ni(C$_6$-DGE)$_6$][Ni(hfacac)$_3$]$_2$ MIL (Figure 2A) from SQUID matches quite well with the theoretical μ_{theo} value (5.31 μ_B, Table 1) and also with that obtained from MSB measurements (5.48 μ_B). However, for the [Mn(C$_6$-DGE)$_6$][Mn(hfacac)$_3$]$_2$ MIL, the μ_{eff} value of 8.31 μ_B

obtained using SQUID appears to be significantly lower than the theoretical value of 10.13 μ_B. The magnetization measurement procedure in SQUID involves a continuous vertical (up and down) movement of the sample-containing glass tube in the magnetic field during data acquisition. Due to its ultra-low viscosity, the sample splattered along the wall of the tube during that movement and a portion of the sample was out of the measurement range, which likely contributed to a significant error in the effective mass of the sample taken during the calculation of μ_{eff}, eventually leading to a lower value. Nevertheless, due to high sensitivity of the technique, magnetic susceptibility measurements using SQUID unambiguously prove that the prepared MIL samples exhibit paramagnetic behavior in the temperature range of 5–300 K without any signature of secondary magnetic phase as well as ordering. It is worth mentioning that a lower μ_{eff} value was also obtained for the $[Co(C_6\text{-}DGE)_6][Co(hfacac)_3]_2$ MIL (Figure S4) due to its low viscosity.

3.5. Miscibility and Solvent Compatibility of DGE-Based MILs with Volatile Organic Solvents.

The solubility of lanthanide and transition metal MILs was investigated in popular traditional organic solvents. A 10 mg mass of each MIL was vigorously mixed with 100 μL of the desired solvent in a 1 mL glass vial to prepare MIL solutions at a concentration of 10% (w/v) MIL-to-solvent ratio. Table 2 shows the solubility of each MIL in 14 polar and nonpolar solvents at different concentrations. All MILs were soluble in water-immiscible solvents, such as benzene, up to concentrations of 50% (w/v) MIL-to-solvent ratio, demonstrating their hydrophobic character. Varying the type of metal center or ligand had no significant influence on the solubility of MILs in organic solvents, such as methanol and 2-propanol, at a concentration of 20% (w/v) MIL-to-solvent ratio. However, MILs composed of C_6-DGE and CycloC$_6$-DGE (MILs **1** to **3** and **7** to **9**) were found to be insoluble in acetonitrile at a concentration of 50% (w/v) MIL-to-solvent ratio compared to those prepared using octyl-based ligands. Additionally, all MILs were insoluble in water at concentrations as low as 0.01% (w/v) MIL-to-solvent ratio.

3.6. Thermal Stability of MILs Containing Multiple Paramagnetic Metal Centers.

To investigate the ability of DGE-based MILs to withstand elevated temperatures without undergoing degradation/decomposition, their thermal stabilities were investigated using TGA, and the thermograms for MILs **1** to **15** are provided in the Supporting Information (Figures S5–S19). Table 2 provides the onset temperature of MIL volatilization/degradation obtained from TGA measurements at 10% weight loss. Degradation temperatures were observed in the range from 163.0 to 264.4 °C, and MILs composed of the C_8-DGE ligand offered slightly higher thermal stabilities compared to those featuring C_6-DGE. MILs composed of CycloC$_6$-DGE degraded at temperatures that were approximately 50 °C lower than the volatilization temperatures of MILs containing the C_6-DGE ligand. Additionally, no significant variations in degradation temperature were observed when Co, Ni, or Mn metals were employed in the cation/anion. However, substituting transition metals with lanthanides in mixed metal MILs (MILs **13** to **15**) resulted in lower volatilization temperatures.

To further investigate the thermal stability of MILs using a more sensitive technique, the solvents were employed as a GC stationary phase and subjected to an oven temperature program from 40 to 200 °C at a ramp rate of 1 °C min^{-1}

and decomposition/degradation products detected using an ultra-sensitive FID.[37] All MIL columns were conditioned for 30 min at 40 °C by passing helium at a constant flow rate of 1 mL min^{-1} prior to running thermal stability measurements. Figure 3 shows the FID response as a function of temperature
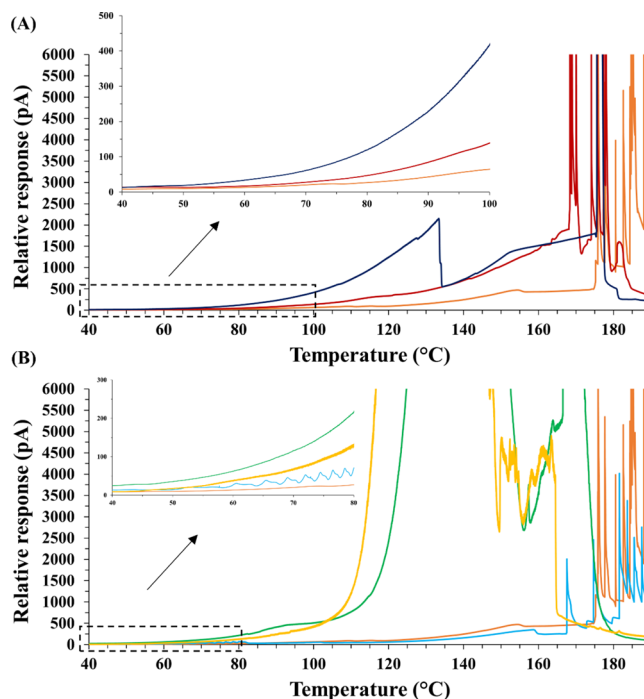

Figure 3. Thermal stability diagram for DGE-based MILs obtained by recording the detector response of a FID as a function of temperature when the MIL is used as a GC stationary phase: $[Co(C_6\text{-}DGE)_6][Co(hfacac)_3]_2$ (red line); $[Co(CycloC_6\text{-}DGE)_6][Co(hfacac)_3]_2$ (blue line); $[Co(C_8\text{-}DGE)_6][Co(hfacac)_3]_2$ (orange line); $[Mn(C_8\text{-}DGE)_6][Mn(hfacac)_3]_2$ (light blue line); $[Co(C_8\text{-}DGE)_6][Gd(hfacac)_4]_2$ (green line); and $[Co(C_8\text{-}DGE)_6][Ho(hfacac)_4]_2$ (yellow line). (A) Effect of cationic ligands on MIL degradation/decomposition and (B) comparison of transition metal MILs with mixed metal combinations.

for select MILs. From Figure 3A, it was observed that the Co MIL composed of the CycloC$_6$-DGE ligand exhibited a higher detector response due to decomposition products entering the detector at lower temperatures compared to the same MIL composed of the C_6-DGE ligand, indicating stronger metal–ligand interactions offered by the straight-chained chelating groups.

However, no significant difference in detector response was observed for MILs **4** to **6**, which varied in the type of transition metal employed in the cation/anion, as shown in Figure 3B. Additionally, the $[Co(C_8\text{-}DGE)_6][Gd(hfacac)_4]_2$ and $[Co(C_8\text{-}DGE)_6][Ho(hfacac)_4]_2$ MILs exhibited very similar responses and volatilized at lower temperatures of approximately 120 °C. Table 2 summarizes the onset temperature of MIL volatilization/degradation obtained using GC-FID measurements. It was observed that the values obtained from these experiments were approximately 30–50 °C lower compared to those measured using TGA. Nevertheless, the trends observed using both techniques were in agreement in most of the cases.

4. CONCLUSIONS

MILs are popular sustainable solvents containing a paramagnetic center in their cation/anion. While several classes of MILs have evolved over the years, most hydrophobic combinations possess viscosities that are several orders of magnitude higher than that of organic solvents. Additionally, most MILs are formed by pairing a quaternary ammonium, phosphonium, or imidazolium salt with a metal-containing anion and provide limited tunability potential, unlike when organometallic complexes are employed as cations. Designing versatile cationic/anionic components can assist in modulating the physico-chemical properties of MILs to avoid the formation of viscous oils or gel-like molten ionic compounds.

In this work, diglycolic acid esters were chelated to transition metals to form bulky cations that were paired with [hfacac$^-$] metal chelates to produce MILs, offering low viscosities below 31.6 cP at 21.7 °C. Embedding paramagnetic centers in both the cation/anion resulted in enhanced magnetic susceptibilities (μ_{eff} of up to 15.56 μ_B) and incorporated characteristics of multiple metal centers in mixed metal MILs. The MILs were found to be highly hydrophobic and were soluble in nonpolar solvents (hexane, benzene, etc.) at concentrations of up to 50% (w/v) MIL-to-solvent ratio and insoluble in water at 0.01% (w/v). In contrast to magnetic nanoparticles that tend to agglomerate and require stabilization, these solvents are chemically and thermally stable at temperatures as high as 190 °C. Considering their high paramagnetic properties and low viscosity, they may have potential in applications that rely on the magnetocaloric effect, such as magnetic refrigeration process. Additionally, the ease with which they can flow expands their scope in separation systems, where other classes of ILs and MILs have limitations. This study provides the framework for the design and synthesis of ultra-low viscosity magnetoactive solvents that incorporate the characteristics of various polar and nonpolar functional moieties, in addition to different types of metal centers, making them accessible to a wider scope of applications beyond their current use.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c03938.

> List of chemicals and reagents, equations used in magnetic susceptibility calculations, images demonstrating the ability of MILs to flow under gravity, Curie−Weiss plots for select MILs, thermograms for solvents obtained using TGA, and ^1H and ^{13}C NMR spectra for diglycolic acid ester ligands synthesized in the study (PDF)

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Notes

The authors declare no competing financial interest.

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