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Synthesis and Characterization of Structurally Diverse Alkaline-Earth Salen Compounds for Subterranean Fluid Flow Tracking

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S Supporting Information

ABSTRACT: A family of magnesium and calcium salenderivatives was synthesized and characterized for use as subterranean fluid flow monitors. For the Mg complexes, di-nbutyl magnesium ($[Mg(Bu^n)_2]$) was reacted with N,N'-ethylene bis(salicylideneimine) (H2-salen), N,N'-bis(salicylidene)-1,2phenylenediamine (H2-saloPh), N,N'-bis(3,5-di-t-butylsalicylidene)-ethylenediamine (H_2 -salo-Bu^t), or N,N'-bis(3,5-di-t-butylsalicylidene)-1,2-phenylenediamine (H_2 -saloPh-Bu^t), and the products were identified by single-crystal X-ray diffraction as



 $\left[(\kappa^3 - (O,N,N'),\mu - (O') \text{saloPh})(\mu - (O),(\kappa^2 - (N,N'),\mu - (O') \text{saloPh})_2(\mu - (O),\kappa^3 - (N,N',O') \text{saloPh}')Mg_4 \right] \cdot 2\text{tol} \quad (1 \cdot 2\text{tol}; \text{ saloPh}' = \text{an}) \cdot (1 \cdot 2\text{tol}; \text{ saloPh}' = 1 \cdot 2\text{tol}) \cdot (1 \cdot 2\text{tol}; \text{ saloPh}' = 1 \cdot 2\text{tol}) \cdot (1 \cdot 2\text{tol}; \text{ saloPh}' = 1 \cdot 2\text{tol}) \cdot (1 \cdot 2\text{tol}$ alkyl-modified saloPh derivative generated in situ), $[(\kappa^4 - (O,N,N',O') \text{saloPh})Mg(py)_2] \cdot py$ (2·py), $[(\kappa^4 - (O,N,N',O') \text{salo-})Mg(py)_2] \cdot py$ (2·py), $[(\kappa^4 - (O,N,N',O')Mg(py)_2] \cdot py$ (2·py), $[(\kappa^$ $\operatorname{Bu}^{t}\operatorname{Mg}(\operatorname{py})_{2}$ (3), $[(\kappa^{4}-(O,N,N',O')\operatorname{saloPh}-\operatorname{Bu}^{t})\operatorname{Mg}(\operatorname{py})_{2}]\cdot\operatorname{tol}(4\cdot\operatorname{tol})$, and $[(\kappa^{3}-(O,N,N'),\mu-(O')\operatorname{saloPh}-\operatorname{Bu}^{t})\operatorname{Mg}]_{2}$ (5), where tol = toluene; py = pyridine. For the Ca species, a calcium amide was independently reacted with H_2 -salo-Bu^t and H_2 -saloPh-Bu^t to generate the crystallographically characterized compounds: $[(\kappa^4-(O,N,N',O')salo-Bu^t)Ca(py)_3]$ (6), $[(\kappa^4-(O,N,N',O')salo-Ph Bu^t$)Ca(py)₃] \cdot py (7 \cdot py). The bulk powders of these compounds were further characterized by a number of analytical tools, where 2-7 were found to be distinguishable by Fourier transform infrared and resonance Raman spectroscopies. Structural properties obtained from quantum calculations of gas-phase analogues are in good agreement with the single-crystal results. The potential utility of these compounds as taggants for monitoring subterranean fluid flows was demonstrated through a series of experiments to evaluate their stability to high temperature and pressure, interaction with mineral surfaces, and elution behavior from a loaded proppant pack.

INTRODUCTION

Accurately monitoring the fluid flow of deep underground reservoirs (water or oil) is imperative to maximize the energy recovery from these wells. Methods developed to track the fluid's movements include radioactive tracers,¹⁻³ DNA fragments,^{4,5} and nanoparticles (i.e., Fe,^{4,6} $Ln/Y_2O_3^7$). Unfortunately, these methods have significant limitations: radioactive materials are not always considered environmentally friendly and do not yield the desired long-term fluid flow information; DNA fragments tend to degrade at the high temperatures and pressures encountered in these underground systems;^{4,5} and nanoparticles have been found to bind to subsurface strata^{6,7} and/or demonstrate poor stability.^{4,6,7} An alternative approach for tracking organic fluids (i.e., oil) being developed in our

laboratories that overcomes these issues utilizes hydrocarbonsoluble compounds that have been intercalated into porous ceramic proppants.⁸ These types of proppants are routinely used in hydraulic fracturing of oil and gas wells, where they are pumped into the fractured reservoir rock, creating high conductivity pathways connecting reservoir fluids to the well bore. As the reservoir fluids flow through the proppants, the molecular taggants will be washed into the "produced" fluids and transported to the surface. For these taggants to be industrially valuable, they must be easily identified and distinguished using standard/mobile analytical tools. This

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concept has been previously demonstrated using phosphonate salts infused into porous ceramic particles in produced reservoir water from hydraulically fractured oil and gas wells.^{9,10}

Metal derivatives of salens, porphyrins, phthalocyanines, and other related multidentate ligands that meet the demanding deep underground system criteria (i.e., solubility, stability, dispersible) have been preliminarily investigated. Of the derivatives noted above, the metal-salen complexes came to the forefront because of the high thermal stabilities reported for this family of compounds.¹¹⁻¹⁵ Additionally, the facile syntheses of salen derivatives is attractive, since the ring substituents can be easily tailored to increase the solubility in the various underground fluids of interest (water vs hydrocarbon). Ligand modifications, especially to the electron-rich rings, and metal selection should result in distinguishable features via vibrational spectroscopy. As large quantities of soluble tags will be necessary to map the fluid flow behavior in real underground systems, the metals employed should be plentiful, nontoxic, and inexpensive.

We therefore selected the alkaline-earth metals for our initial efforts, and this report details the syntheses and characterization of a family of magnesium (Mg) and calcium (Ca) salen compounds. The salen ligands (H_2 -saloR'-R; Figure 1a–d)



Figure 1. Schematic structures of H₂-saloR'-R derivatives: (a) H₂-salen, (b) H₂-saloPh, (c) H₂-salo-Bu^t, (d) H₂-saloPh-Bu^t, and (e) dihedral angles analyzed: (i) N–C C–N, (ii) N…N C–C, and C…M… C.

studied include: (a) *N*,*N'*-ethylene bis(salicylideneimine) (H₂salen), (b) *N*,*N'*-bis(salicylidene)-1,2-phenylenediamine (H₂saloPh), (c) *N*,*N'*-bis(3,5-di-*t*-butylsalicylidene)-ethylenediamine (H₂-salo-Bu^t), and (d) *N*,*N'*-bis(3,5-di-*t*-butylsalicylidene)-1,2-phenylenediamine (H₂-saloPh-Bu^t). The products isolated from the reaction of di-*n*-butyl magnesium (Mg(Buⁿ)₂; eq 1) with the H₂-saloR'-R derivatives were crystallographically identified as $[(\kappa^3-(O,N,N'),\mu-(O')saloPh)(\mu-(O),(\kappa^2-(N,N'),\mu-(O')saloPh)_2(\mu-(O),\kappa^3-(N,N',O')saloPh')Mg_4]\cdot2tol$ (1·2tol; saloPh' = an alkyl-modified saloPh derivative generated in situ), $[(\kappa^4-(O,N,N',O')saloPh)Mg(py)_2]\cdotpy$ (2·py), $[(\kappa^4-(O,N,N',O')saloPh Bu^t)Mg(py)_2]\cdottol$ (4·tol), and $[(\kappa^3-(O,N,N'),\mu-(O')saloPh-$ Bu^{*t*})Mg]₂ (**5**) where tol = toluene and py = pyridine. For the Ca species, calcium bis(trimethylsilyl)amide ($[Ca(NR_2)_2]$; eq 2) was independently reacted with H₂-salo-Bu^{*t*} and H₂-saloPh-Bu^{*t*} to generate the crystallographically characterized complexes $[(\kappa^4-(O,N,N',O')\text{salo-Bu}^t)Ca(py)_3]$ (**6**) and $[(\kappa^4-(O,N,N',O')\text{-saloPh-Bu}^t)Ca(py)_3]$ ·py (7·py). These compounds were fully characterized using a variety of analytical techniques. Additionally, molecular modeling of the compounds was undertaken to analyze the impact that the different ligand modifications had on the degree of charge transfer between the metal ion and the organic components (saloR'-R moieties and py ligands). Electronic structure calculations were validated by comparing geometric properties with those obtained by single-crystal diffraction experiments.

$$\begin{split} \left[Mg(Bu^{n})_{2} \right] + H_{2}\text{-saloR'-R''} &\rightarrow \left[(\text{solv})_{x}Mg(\text{saloR'-R}) \right] \\ (1) \\ \left[Ca(NR_{2})_{2} \right] + H_{2}\text{-saloR'-Bu}^{t} \rightarrow \left[(\text{solv})_{x}Ca(\text{saloR'-Bu}^{t}) \right] \end{split}$$

 $R = Si(CH_3)_3;$ $R' = C_2H_4, C_6H_4;$ $R'' = H, 2, 4-Bu^t$

With this unique set of precursors available, preliminary investigations into the retention of the structure under simulated deep well conditions were investigated, including thermal/pressure, interaction with surfaces (SiO₂ columns), and elution data from the proppant. The potential tracker properties for select compounds were determined and are briefly discussed.

EXPERIMENTAL SECTION

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glovebox techniques unless otherwise discussed. All chemicals were used as received (from Aldrich and Alfa Aesar) without further purification, including: methanol (MeOH; anhydrous, 99.8%), diethyl ether (Et₂O, anhydrous, 99.7%), pyridine (py; anhydrous, 99.8%), tetrahydrofuran (THF; anhydrous, \geq 99.9%), toluene (tol; anhydrous, 99.8%), N,N'bis(salicylidene)ethylenediamine (H2-salen; 98%), N,N'-bis-(salicylidene)-1,2-phenylenediamine (H₂-saloPh; 97%), calcium iodide (CaI₂), 1.0 M di-*n*-butyl magnesium solution ([Mg(Buⁿ)₂] in heptane), potassium bis(trimethylsilyl)amide (KNR₂), 3,5-di-tertbutyl-2-hydroxybenzaldehyde (99%), ethylene diamine (99%), pyridine- d_5 (py- d_5 ; \geq 99.5 atom % D), and chloroform-d (CDCl₂; 99.8 atom % D). Ortho-phenylenediamine (98%) was obtained from Acros Organics. Calcium bis(trimethylsilyl)amide ([Ca(NR₂)₂]) was synthesized from the reaction of CaI₂ and 2 equiv of KNR₂ in THF.¹⁶ Dried crystalline materials were used for all analytical analyses. The porous proppant used was provided by Carbo Ceramics, Inc., and is available from them under the product name 20/40 CarboUltraLite.

Fourier transform infrared (FTIR) data were collected on a Nicolet 6700 FTIR spectrometer using a KBr pellet press under a flowing atmosphere of nitrogen or with iD7 ATR accessory mounted with a monolithic diamond crystal. Spectra of select species are shown in Supporting Information (Figures S1 and S2). Elemental analyses were collected on a PerkinElmer 2400 Series II CHNS/O Analyzer with samples prepared in an argon-filled glovebox. Melting point data were collected using a Stanford Research Systems Optimelt MPA100. Raman spectra were obtained using a Thermo Scientific DXR Smart Raman instrument. All NMR samples were prepared under an argon atmosphere and flame-sealed using crystalline material at as high a concentration as possible. Spectra were collected on a Bruker Avance 500 NMR spectrometer under standard experimental conditions: ¹H analysis was performed with a 4 s recycle delay at 16 scans; ¹³C analysis was performed with a 10 s recycle delay with a minimum of 64 scans. Alternatively, a Bruker Fourier 300 HD spectrometer or a

Magritek Spinsolve Phosphorus benchtop spectrometer was also used. All spectra were referenced to the appropriate residual protonated species in the solvent. The Thermogravimetric analysis (TGA)/ differential scanning calorimetry (DSC) analyses were obtained on a Mettler Toledo model TGA/DSC 1. UV–vis absorbance spectral data were collected on a Photonics CCD Array UV–vis Spectrophotometer. All experiments were conducted under an argon atmosphere at a heating rate of 10 °C min⁻¹ from room temperature to 750 °C in an alumina crucible.

Ligand Synthesis. H₂-salo-Bu^t. 3,5-Di-tert-butyl salicylaldehyde (4.68 g, 20.0 mmol) and ethylene diamine (0.600 g, 9.98 mmol) were added to a 500 mL round-bottom flask containing MeOH (~225 mL). After it was stirred at 65 °C for 17 h, the reaction was allowed to cool to room temperature. The resulting precipitate was isolated by filtration, rinsed with Et₂O (3×20 mL), and dried in an oven at 100 °C for 24 h affording an off white/light yellow powder. Yield 96.1% (4.73 g). FTIR (cm⁻¹; iD7 ATR): 3254 (w(br), -OH), 3051 (w), 2956 (s), 2867 (m), 1626 (s, C=N), 1594 (m), 1464 (s), 1438 (s), 1392 (m), 1360 (s), 1252 (m), 1172 (s), 1040 (s), 879 (s), 829 (s), 773 (s), 709 (s), 644 (s). ¹H NMR (500.1 MHz, CDCl₃): 13.64 (s, 2H, -OH), 8.40 (s, 2H, -CHN-), 7.36 (d, 2H, C₆H₂(C(CH₃)₃)₂), 7.08 (d, 2H, $C_6H_2(C(CH_3)_3)_2$), 3.94 (s, 4H, $N(CH_2)_2N$); 1.45 (s, 18H, $C(CH_3)_3$; 1.30 (s, 18H, $C(CH_3)_3$). Anal. Calcd for $C_{32}H_{48}N_2O_2$ (MW = 492.75): C, 78.00; H, 9.82; N, 5.69. Found: C, 78.43; H, 9.96; N, 5.57%. mp 184-187 °C.

*H*₂-saloPh-Bu[†]. 3,5-Di-tert-butyl salicylaldehyde (2.24 g, 9.56 mmol) and *o*-phenylenediamine (0.59 g, 5.46 mmol) were added to a 250 mL round-bottom flask containing 75 mL of MeOH. After it was stirred at 65 °C for 17 h, the reaction was allowed to cool to room temperature. The resulting precipitate was isolated by filtration, rinsed with Et₂O (3 × 20 mL), and dried in an oven at 100 °C for 24 h. This afforded a light-yellow powder. Yield: 72.1% (1.95 g). FTIR (cm⁻¹; iD7 ATR): 3368 (w(br), −OH), 3056 (w), 2951 (s), 2905 (m), 2866 (m), 1805 (w), 1615 (s, C=N), 1570 (s), 1479 (m), 1438 (s), 1360 (s), 1251 (m), 1169 (s), 1104 (m), 973 (m), 877 (m), 820 (m), 755 (s), 643 (m). ¹H NMR (43 MHz, CDCl₃): 13.52 (s, 2H, −OH), 8.66 (s, 2H, −CHN-), 7.18−7.41 (m, 4H, C₆H₂(C(CH₃)₃)₂), 1.45 (s, 18H, −C(CH₃)₃). Anal. Calcd for C₃₆H₄₈N₂O₂ (MW = 540.79): C, 79.96; H, 8.95; N, 5.18. Found: C, 80.40; H, 8.68; N, 4.97%. mp 194−197 °C.

General Mg-Salen Reaction. In an inert atmosphere glovebox, a preweighed sample of the desired H_2 -saloR'-R was added to a stirring solution of $[Mg(Bu^n)_2]$ in toluene. After it was stirred for 12 h, py was added (except for 5), and the reaction was stirred for at least an additional hour. This reaction was set aside until X-ray quality crystals grew.

 $[(\kappa^{4}-(O,N,N',O')saloPh)Mg(py)_{2}]\cdot py (2\cdot py). [Mg(Bu^{n})_{2}] (0.95 \text{ mL})$ 0.95 mmol), H₂-salo-Ph (0.30 g, 0.95 mmol) in toluene (~5 mL). Reaction turns red-orange in color; powder dries to a pale orange color. After it was stirred for 12 h, py addition yielded a red product. Yield 84.2% (0.46 g). FTIR (KBr, cm⁻¹) 3053(s), 2014(s), 2955(s), 2924(s), 2869(m), 1611(s), 1583(s,sh), 1546(s), 1526(s), 1483(s,sh), 1469(s), 1388(s), 1302(s), 1247(w), 1220(w), 1180(s), 1147(s), 1125(m), 1107(m), 1077(w), 1041(m), 1001(m), 976(w), 918(m), 856(w), 840(w), 801(w), 749(s), 701(m), 618(w,sh), 605(w), 635(m). ¹H NMR (500.1 MHz, py- d_5) δ 9.09 (1H, s(br), NC₅H₅), 8.70 (2H, s(br), -C(H) = N-, NC_5H_5), 7.80–7.79 (1H, mult., OC_6H_5), 7.54 (1H, t, $J_{\rm H-H}$ = 7.6 Hz, OC₆H₅), 7.48 (1H, d, $J_{\rm H-H}$ = 3.9 Hz, OC_6H_5), 7.33 (1H, t, J_{H-H} = 7.6 Hz, NC_5H_5), 7.24–7.31(1H, mult., OC_6H_5 , N-C₆H₅), 7.21 (2H, t, $J_{H-H} = 7.4$ Hz, OC_6H_5 , N-C₆H₅), 6.55 (1H, t, J_{H-H} = 7.4 Hz, O-C₆H₅). Anal. Calcd for C₃₀H₂₄MgN₄O₂ (2, MW = 496.85): C, 72.52; H, 4.87; N, 11.28. Found: C, 71.59; H, 5.82; N, 8.27%.

 $[(\kappa^{4}-(O,N,N',O')salo-Bu^{t})Mg(py)_{2}]$ (3). $[Mg(Bu^{n})_{2}]$ (2.03 mL, 2.03 mmol), H₂-salo-Bu^t (1.00 g, 2.03 mmol) in toluene (~15 mL) and py (~1.5 mL). Reaction turns yellow in color; powder dries to a light brown. Yield 90.0% (1.23 g). FTIR (KBr, cm⁻¹): 2956(s), 2868(s), 1629(s), 1545(w,sh), 1528(m), 1467(s), 1441(s), 1414(m), 1391(m), 1360(m), 1336(w), 1300(w), 1275(w), 1275(w,sh), 1257(m), 1233(w), 1217(w), 1200(w), 1160(m), 1089(w), 1070(w), 1037(w),

986(w), 909(w), 878(w), 852(w,sh), 833(w), 806(w), 793(w), 757(w), 744(w), 702(m), 621(w), 476(w), 432(w). ¹H NMR (500.1 MHz, py- d_5) δ 8.70 (1H, d, $J_{H-H} = 2.1$ Hz, NC₅H₅), 8.31 (1H, s, -C(H)=N-), 7.67 (1H, t, $J_{H-H} = 2.6$ Hz, OC₆H₂Bu^t₂), 7.52 (0.5H, t, $J_{H-H} = 1.7$ Hz, NC₅H₅), 7.29 (1H, d, $J_{H-H} = 2.6$ Hz, OC₆H₂Bu^t₂), 7.17 (1H, t, $J_{H-H} = 1.7$ Hz, NC₅H₅), 3.39 (2H, s, -N-CH₂-), 1.59 (9H, s, OC₆H₂(C(CH₃)₃)₂), 1.23 (9H, s, OC₆H₂(C-(CH₃)₃)₂). Anal. Calcd for C₄₂H₅₆MgN₄O₂ (MW = 673.24): C, 74.93; H, 8.38; N, 8.32. C₃₇H₅₁MgN₃O₂ (MW = 594.14; 3 - 1 py): C, 74.80; H, 8.65; N, 7.07. Found: C, 75.43; H, 8.35; N, 6.45%.

 $[(\kappa^4-(O,N,N',O')saloPh-Bu^t)Mg(py)_2]$ -tol (4-tol). $[Mg(Bu^n)_2]$ (1.85) mL, 1.85 mmol), H₂-saloPh-Bu^t (1.00 g, 1.85 mmol) in toluene (~15 mL) with py (~1.5 mL). Yield 93.7% (1.41 g). Reaction turns yellow in color; powder dries to a light brown. FTIR (cm⁻¹): 3071 (w); 2995 (w); 2951 (s); 2904 (m); 2864 (m); 1604 (s); 1578 (s); 1546 (m); 1464 (s); 1438 (s); 1387 (s); 1360 (s); 1248 (m); 1191 (m); 1159 (s); 1134 (s); 1109 (m); 1042 (m); 978 (m); 836 (m); 795 (s); 746 (s); 699 (s). ¹H NMR (500.1 MHz, py- d_5) δ 9.25 (1H, s(br), NC₅H₅), 8.70 (2H, s(br), -C(H) = N, NC_5H_5), 7.90–7.88 (1H, mult., $OC_6H_2Bu_2^t$), 7.68 (1H, t, $J_{H-H} = 7.3$ Hz, $OC_6H_2Bu_2^t$), 7.45 (1H, t, $J_{\rm H-H} = 7.6 \, \text{Hz}, \, \text{NC}_5 H_5), \, 7.33 - 7.22(1 \, \text{H}, \, \text{mult.}, \, \text{OC}_6 \, H_2 \, \text{Bu}_2^t, \, \text{N} - \text{C}_6 \, H_5),$ 7.18 (2H, t, $J_{H-H} = 7.4$ Hz, $OC_6H_2Bu_2^t$), 1.78 (9H, s, $OC_6H_2(C (CH_3)_3)_2$, 1.31 (9H, s, $OC_6H_2(C(CH_3)_3)_2)$. Anal. Calcd for $C_{53}H_{64}MgN_4O_2$ (MW = 813.43): C, 78.26; H, 7.93; N, 6.89. $C_{99}H_{120}Mg_2N_8O_4$ (MW = 1534.71; 4 + 1/2 tol): C, 77.48; H, 7.88; N, 7.30. Found: C, 77.03; H, 8.62; N, 6.55%.

 $[(\kappa^3 - (O, N, N'), \mu - (O')saloPh-Bu')Mg]_2$ (5). $[Mg(Bu^n)_2]$ (0.46 mL, 0.46 mmol), H₂-saloPh-Bu^t (0.25 g, 0.46 mmol) in toluene (~15 mL). Yield 92.2% (0.24 g). Reaction turns dark brown in color; powder dries to orange. FTIR (cm⁻¹): 2956(s), 2905(s), 2867(s), 1614(s), 1581(s), 1528(s), 1463(s), 1438(m), 1409(w), 1385(m), 1360(m), 1333(w), 1259(s), 1197(m), 1167(s), 1136(w), 1108(m), 1025(w), 974(w), 927(w), 872(w), 834(w), 795(w), 749(m), 695(w), 637(w), 535(w), 522(w). Anal. Calcd for C₇₂H₉₂Mg₂N₄O₄ (5, MW = 1126.16): C, 76.79; H, 8.23; N, 4.98. Found: C, 76.60; H, 8.31; N, 4.64%.

General Ca-Salen Reaction. In an inert atmosphere glovebox, a preweighed sample of the desired H_2 -saloR'-R was added to a stirring solution of $[Ca(NR_2)_2]$ in toluene. After it was stirred for 12 h, py was added, and the reaction was stirred for at least 1 h and then set aside with the cap removed until X-ray quality crystals grew.

[(κ^4 -(*O*,*N*,*N*',*O*')*salo-Bu*[†])*Ca*(*py*)₃^{*j*}] (6). [Ca(NR₂)₂] (0.732 g, 2.03 mmol), H₂-salo-Bu^t (1.00 g, 2.03) in toluene (~15 mL) and py (~1.5 mL). The reaction turns pale yellow in color; powder dried to off-white powder. Yield 89.8% (1.40 g). FTIR (cm⁻¹): 3060 (w); 2956 (s); 2906 (m); 2867 (s); 1624 (s, C=N); 1525 (m); 1464 (s); 1438 (s); 1392 (m); 1359 (s); 1270 (s); 1252 (s); 1200 (m); 1154 (m); 1041 (s); 973 (s); 931 (s); 879 (s); 774 (s); 728 (s); 694 (s); 645 (m). ¹H NMR (500.1 MHz, py-*d*₅) δ 8.70 (0.5H, d, *J*_{H-H} = 2.7 Hz, NC₃H₅), 8.31 (1H, s, -C(H)=N-), 7.64 (1H, s(br), OC₆H₂Bu^t₂), 7.54 (0.5H, t, *J*_{H-H} = 7.5 Hz NC₃H₅), 7.29 (1H, s(br), OC₆H₂Bu^t₂), 7.18 (0.5H, t, *J*_{H-H} = 7.5 Hz, NC₅H₅), 3.30 (2H, s, -N-CH₂-), 1.37 (9H, s, OC₆H₂(C(CH₃)₃)₂), 1.33 (9H, s, OC₆H₂(C(CH₃)₃)₂). Anal. Calcd for C₄₇H₆₁CaN₅O₂ (6, MW = 768.12): C, 73.49; H, 8.01; N, 9.12. Found: C,72.79; H, 8.22; N, 9.17%.

[(κ^4 -(*O*,*N*,*N*,*O*')*saloPh-Bu*[†])*Ca*(*py*)₃]·*py* (7·*py*). [Ca(NR₂)₂] (0.667 g, 1.85 mmol), H₂-saloPh-Bu^t (1.00 g, 1.85 mmol) in toluene (~15 mL) and py (~1.5 mL). The reaction turns dark yellow in color; powder dried to yellow-orange powder. Yield 93.2% (1.27 g). FTIR (cm⁻¹): 3060 (w); 2992 (w); 2946 (m); 2904 (m); 2866 (m); 1594 (s, C=N); 1573 (s); 1518 (m); 1436 (s); 1381 (m); 1358 (m); 1236 (m); 1195 (s); 1149 (s); 1032 (m); 976 (m); 875 (m); 796 (s); 744 (s); 699 (s). ¹H NMR (500.1 MHz, py-*d*₅) δ 8.70 (mult., NC₅H₅), 8.55 (2H, s, CH=N), 7.63 (2H, s, OC₆H₂Bu^t₂), 7.55(2H, mult, NC₅H₅), 7.33 (2H, s, OC₆H₂Bu^t₂), 7.19 (mult. NC₅H₅), 7.05 (4H, s, C₆H₄), 1.51 (9H, s, OC₆H₂Bu^t₂), 1.37 (9H, s, OC₆H₂Bu^t₂). Anal. Calcd for C₅₆H₆₆CaN₆O₂ (7·*py*, MW = 895.26): C, 75.13; H, 7.43; N, 9.39. C₅₁H₆₁CaN₅O₂ (7 · *py*, MW = 737.06): C, 74.96; H, 7.66; N, 7.60. Found: C, 75.52; H, 8.10; N, 7.34%.

Table 1. Select	(Average) Metrical Data ^a	(Experimental and	d Calculated) for $1-7$
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		distances (Å)		angle (deg)				
compd	Mg-O _{sal}	Mg-N _{sal}	Mg-N _{py}	O-M-O ^b	N-M-N ^b	O-M-N ^b	O-M-N' ^b	N _{py} -M-N _{py}
2	1.97	2.16	2.31	109.12	76.48	87.22	163.49	179.73 ^c
								163.47
calcd	1.91	2.11	2.24	103.68	77.88	89.14	166.73	179.73
3	1.96	2.16	2.27	116.07	75.48	84.39	158.93	177.37
calcd	1.97	2.17	2.24	114.83	77.08	84.28	160.41	176.59
4	1.94	2.15	2.30	107.43	77.15	87.81	164.47	177.26
calcd	1.96	2.16	2.24	110.10	77.31	86.29	163.59	176.28
4a	1.93	2.13	2.13	101.47	76.38	87.02	154.86	
5	1.93 (t)	2.13		115.30 (µ-t)	76.38	85.79	142.73(t)	
							160.17 (µ)	
	2.03 (µ)			106.53 (µ'-t)				
				84.57 (µ-µ)				
calcd	1.93 (t)	2.14		85.12 (µ-t)	75.63	85.67	138.27 (t)	
	2.01 (µ)			105.91 (µ'-t)			159.13 (µ)	
				119.16 (µ–µ)				
6	2.29	2.56	2.52	153.11	67.30	70.77	135.76	176.94, 88.47, 88.47
calcd	2.27	2.52	2.54	151.94	68.50	71.89	135.36	175.34, 86.23, 89.11
7	2.26	2.51	2.57	148.09	64.88	71.99	136.23	171.21, 107.23, 81.66
calcd	2.29	2.52	2.54	147.68	66.79	72.98	139.20	168.31, 81.21, 87.11
$f'(t)$ = terminal, (μ) = bridging. ^b As within a salen moiety. ^c Two molecules in the unit cell.								

General X-ray Crystal Structure Information. For 1, 2, 4, 6, and 7, single crystals were mounted onto a loop from a pool of Fluorolube or Parabar 10312 and immediately placed in a cold N₂ vapor stream on a Bruker AXS diffractometer employing an incidentbeam graphite monochromator, Mo K α radiation ($\lambda = 0.710$ 70 Å) and a SMART APEX CCD detector. Indexing and frame integration were performed using the APEX-III software suite. Absorption correction was performed using face-indexing (numerical method) also within the APEX-III software. The structures were solved using SHELXL-2016/6 and refined using OLEX2 version 1.2.¹⁷ All final CIF files were checked using the CheckCIF program (http://www.iucr.org/). Specific issues with the characterization of 1, 3, and 5 were due to the limitation of the Mo source employed. A rational route to 1 has not been realized, yet, but it is reported for completeness; however, structural issues with 1 were due to poor diffraction.

For compounds **3**, **4a**, and **5** alternative single-crystal X-ray systems were employed with substantially improved results. These were collected on either a Bruker Ultra system with a Mo rotating-anode source with Helios multilayer optics (no graphite monochromator) and an APEXII CCD detector or a system employing a Rigaku FR-X Cu rotating-anode source with Helios multilayer optics and a Platium135 CCD detector on a Bruker D8 platform.

Additional information concerning the data collection and final structural solutions can be found in the Supporting Information or by accessing CIF files through the Cambridge Crystallographic Data Base. The unit cell parameters for the structurally characterized compounds 1–7 are listed in the Supporting Information.

Computational Modeling. Gas-phase electronic structure calculations were performed on individual M–L complexes using Gaussian 09^{18} at the density functional theory (DFT) level. The M062X hybrid functional¹⁹ was used along with the cc-pVDZ basis set^{19–22} for all atoms. The M062X functional was used to model spectroscopic properties of magnesium complexes.^{23,24} This combination of DFT methods has previously been found to yield excellent agreement with experimental structures of related M–L compounds.^{25,26} All atoms were allowed to relax in all structures except **2**, since the ligand phenyl rings tilted significantly out of plane. Instead, this structure was initially optimized without py ligands, and then these atoms were held fixed while the py ligands were optimized. The resulting structure is lower in energy and more consistent with the other Mg complexes (**3–5**). After geometry optimization, partial atomic charges for all complexes were calculated using the CHELPG method,²⁷ with default atomic radii for C, H, N, O, and Mg atoms and a radius of 2.31 Å for Ca atoms.²⁸ Table 1 shows the excellent agreement in metrical data between the crystal structures and DFT-optimized structures, validating the quality of the DFT models for these hybrid compounds. The atomic coordinates and CHELPG charges of Gaussian-optimized structures can be found in the Supporting Information.

Proppant Loading. The pore volume of the proppant is reported to be 0.112 mL/g, and no more than 90% of pore volume was to be occupied by complex in solution during the impregnation process. Therefore, the precursor loading was between 2 and 6 wt % using an infusion (or impregnation) process that is similar to that used in the preparation of heterogeneous catalysts. To a preweighed vial, the desired amount of metal salen complex was added to 10 mL of toluene (referred to as saloR-Bu^t solution). The proppant was weighed (10.0 g) into a separate vial, and 0.8 mL of saloR-Bu^t solution was added dropwise to the vial containing proppant and adsorbed into the pores. After each addition, the vial was shaken, and the excess toluene was removed in vacuo. This process was repeated, until the desired wt % loading was achieved. Loadings: Compound 3 (0.479 g) loading achieved 4.79 wt % of 3 in proppant, Compound 4 (0.632 g) loading achieved 6.32 wt % of 4 in proppant, and compound 7 (0.648 g) loading achieved 6.48 wt % of 7 in proppant.

Column Preparation/Elution. Sand (~30 g; ACS grade, Aldrich) was added to a column (226 mm) and saturated with toluene (20 mL). Each compound (0.100 g) was dissolved in toluene (50 mL), stirred for 30 min, and added to the column in aliquots (10 mL) until depleted. The sample flask was then rinsed with toluene (~50 mL), which was added to the column. This was followed by an additional toluene (~50 mL) wash. Every step was run at a flow rate of 0.065 mL/sec. The product was identified by FTIR spectral data. Recovered yields for: 2, 100% (0.10 g); 3, (100%; 0.10 g); 4, (100%; 0.10 g); 5, 74% (0.074 g).

Solvothermal Processing. The stability of this family of compounds under the high pressure and temperatures was evaluated using a solvothermal (SOLVO) approach. For 2–7, a 0.10 g sample was placed into a Teflon liner of a Parr Digestion bomb in 20 mL of solvent (toluene or dodecane), sealed, and heated to a preset temperature (120 or 180 °C) for 24 h. After this time, the residual product was isolated by centrifugation, washed with hexanes (three times), and characterized via FTIR spectroscopy (see Supporting Information) to evaluate structure retention.

Elution Studies. Laboratory experiments designed to mimic fluid flow through hydraulically fractured zones in a subsurface well that contain a ceramic proppant are available. In general, the experimental setup uses a cartridge pump to send the desired solvent fluid (either aqueous or hydrocarbon) at a constant rate through a small "proppant pack" to a fraction collector. The proppant pack consists of porous proppants that have been infused with the metal salen compounds, which are packed into a plastic syringe equipped with a fine mesh proppant retention screen at the entrance tip. The pore volume-a measure of the fluid volume within the pack of proppant pellets-is measured. The proppant pack is then sealed at the top with a rubber septum to generate pressure to force the exiting fluid into tubing for transport to the collection test tubes in the fraction collector. Samples were collected over 40+ pore volumes, and the concentrations of metal complexes in the samples were measured by atomic absorption spectrophotometry (AAS) after 4, 20, and 40 pore volumes had passed over the proppant pack. A photograph of the elution testing setup is shown in Figure S3 of the Supporting Information.

For the initial efforts, compound 4 was analyzed. To quantify the concentration of Mg in the samples recovered from the elution test, a PerkinElmer PinAAcle 900T Atomic Absorption Spectrophotometer was used in flame mode. Standard solutions containing known concentrations of Mg were prepared from mesityl magnesium bromide (1 M in THF; Aldrich) diluted with *n*-propyl alcohol and Isopar L (final solutions contained 20 vol % Isopar L). The Isopar L was added to standards in order to match the matrix in the samples (Isopar L was the solvent used in the elution studies, and all samples were diluted 4:1 with *n*-propyl alcohol before AAS analysis).

RESULTS AND DISCUSSION

A search of the structure literature reveals that surprisingly few alkaline-earth salen derivatives have been reported.²⁹ Of the 22 compounds structurally characterized with at least one alkalineearth metal coupled to a salen backbone, the majority of the family members are heterometallic species with the alkalineearth cations located externally to the salen cavity, including: Mg-Cu, $^{30-34}$ Mg-Ni, 35 Ca-Ni, 35 Ca-U, 36 Ca-Cu, 37,38 Sr-Cu, 39 Ba-Cu, 40,41 Ba-Ni, 42,43 and Ba-Fe. 44 Only six homometallic compounds have been reported: [Be(μ -(κ^4 -(O,N,N',O') salen))]₂·H₂O,⁴⁵ bis(μ -3,3'-(ethane-1,2-div) bis-(iminiomethyl ylidene)) bis(2-oxybenzoate))diaqua, dimagnesium hexahydrate),⁴⁶ aqua, methanol-(ethylendiamine- $N_{,N'}$ -bis- $\begin{array}{ll} (2\mbox{-aldimino-4-methyl-6-formylphenolato})) & magnesium, \end{tabular} \\ (THF)(HOEt)_2 Ca(\kappa^4\mbox{-}(O,N,N'O')\mbox{salo-Bu}^{t}, \end{tabular}^{48} & (DME)Ca(\kappa^4\mbox{-}) \\ \end{array}$ (O,N,N'O')saloCy-Bu^t),⁴⁹ where saloCy-Bu^t = bis(3,5-di-t-butylsalicylidene)cyclohexane-1,2-diamine, (HOEt)₃Sr(κ^4 -(O,N,N'O')salo-Bu^t).⁴⁸ It is of note that $[Mg(salen)]_2$ and [Mg(salo-Ph)]₂ were reported from the reaction of [Mg- $(CH_2C_6H_5)_2$ and the respective Schiff-base; however, these products were not crystallographically characterized.³⁵

We were initially interested in Mg and Ca due to their ubiquity in nature and low cost; however, the diversity of the coordination numbers (CNs) of the Mg and Ca compounds (CN ranges from 4 through 7), the number and types of solvent molecules bound, the torsional angle of the salen backbone, and the lack of homoleptic Mg derivatives indicated that a study of this family of compounds was necessary prior to their use as taggants. Therefore, the syntheses and characterization of Mg and Ca derivatives was undertaken. Once isolated and modeled, their analytical properties were obtained to determine if they could be individually identified by simple spectroscopic means, a key feature for the possible use as monitors in deep well fluid systems.

Mg Complexes. Following the report by Corazza et al. on the successful substitution of Mg into the salen ring through an

alkyl derivative,⁵⁰ the reaction of $[Mg(Bu^n)_2]$ with the commercially available H₂-salen or H₂-saloPh was undertaken in toluene (eq 1). For the H₂-salen ligand, the products formed were found to be insoluble in toluene, but upon addition of the strong Lewis base py, clear, orange solutions could be obtained at elevated temperatures. All attempts to generate single crystals yielded only amorphous powders. Switching to the H₂-saloPh ligand led to a clear, dark-orange solution from warm toluene. The crystals that grew upon slow cooling were identified as compound 1 (shown in Figure 2).



Figure 2. Structure plot of **1**. The heavy-atom thermal ellipsoids are drawn at 30% level, with C atoms drawn as ball and stick and H atoms omitted for clarity.

Initial inspection of the structure of 1 reveals four "Mg(saloPh)" moieties that are interconnected through the oxygen atoms from the phenoxide rings: two terminal (one bridges) and two internal (both bridge). The inclusion of the *n*butyl group results in a chain of $[(\mu - O)-Mg]_4$ with two trigonal bipyramidal ($\tau = 0.37$)⁵¹ and two pseudo-octahedral (OC-6) bound Mg metal centers. Upon closer examination of the second saloPh ligand, surprisingly, an *n*-butyl group was solved, branching off the carbon of the "Ph-C(34)=N(4)-Mg(2)" moiety. This indicates that a C-C bond was formed in this simple reaction. This mechanism is not fully understood, but the use of the basic $[Mg(Bu^n)_2]$ may lead to deprotonation of the Ph-C(H)=N fragment. Isolation of crystals from this reaction have not been easily reproducible, and the structure suffers from weak diffraction. This compound is not included in the Experimental Section, as an established route to the molecule is not available; however, the structure properties are reported (see Table S1 in Supporting Information) due to its unique tetranuclear nature and the unexpected C-C bond formation.52

Alternatively, the product isolated from the Lewis basic solvent py was found to be the mononuclear compound **2** (Figure 3). Compound **2** is the first report of a structurally characterized, alkaline-earth salen derivative with a bound py solvent molecule. The coordination of the Mg is best described as pseudo octahedral (OC-6) using the full complement of available binding sites on the saloPh-Bu^t(κ^4 -O,N,N',O') ligand along with two trans bound py solvent molecules.



Figure 3. Structure plot of $2 \cdot \text{py}$. The heavy-atom thermal ellipsoids are drawn at 30% level, with C atoms drawn as ball and stick and H atoms omitted for clarity. The two molecules per unit cell are shown.

Salen derivatives with t-butyl groups on the rings were of interest due to their expected increased solubility in organic solvents. Both the ethyl^{53,54} and phenylene⁵⁵ diamine derivatives (Figure 1c,d) were synthesized following literature routes,⁵³⁻⁵⁸ wherein 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was condensed with ethylene-1,2-diamine or o-phenylene-1,2diamine forming N,N'-bis(3,5-di-t-butylsalicylidene)-ethylenediamine (H₂-salo-Bu^t, Figure 1c) or N,N'-bis(3,5-di-t-butylsalicylidene)-1,2-phenylenediamine (H₂-saloPh-Bu^t: Figure 1d), respectively. Once isolated and characterized, these ligands were reacted with $[Mg(Bu^n)_2]$, following eq 1. The products isolated were identified by single-crystal X-ray diffraction studies as the monomeric species 3 and 4 (see Figures 4 and 5a, respectively). The saloR-Bu^t derivatives act in the same tetradentate manner binding through the κ^4 -O,N,N',O' atoms with trans axial py molecules.

Attempts to reproduce an improved crystal of 4 led to the isolation of 4a (Figure 5b). While the binding mode of the salo-Bu^t to the Mg for both compounds are identical, only one py solvent molecule was solved bound to the Mg cation of 4a. This limited solvation places the Mg in a 5-coordinate square base pyramidal ($\tau = 0$) geometry. A rational route to the mono- (4a) versus the disubstituted (4) has not been discerned, as of yet. Since the ability to bind a variable number of solvent molecules is unexpected and difficult to control, the structure parameters (see Table S1 in Supporting Information) are reported to allow for ease of identification. There are some differences in the metrical data of 4 and 4a. In particular, the Mg-N distance of the disubstituted species is over 0.15 Å longer. This weaker interaction is also reflected in the 6° and 10° larger bond angles of O-M-O and O-M-N, respectively. On the basis of these metrical data, the number or type of solvent bound to the metal may play a bigger role in the final stability of these compounds in real-world efforts than originally anticipated.

It was of interest to determine if the solventless structures for the saloPh- Bu^t -Mg derivatives could be obtained and what



Figure 4. Structure plot of **3**. The heavy-atom thermal ellipsoids are drawn at 30% level, with C atoms drawn as ball and stick and H atoms omitted for clarity.

their structural arrangement would be. Following the same reaction pathway noted above but omitting the addition of py led to the crystallization of compound **5**. This compound was characterized by single-crystal X-ray diffraction as a dinuclear complex (Figure 6). For **5**, each 5-coordinated Mg was solved in a square base pyramidal geometry ($\tau = 0.96$) binding in a κ^3 -(O,N,N'), μ -(O') chelation mode, where the second O atom from each saloPh-Bu^t bridges two Mg centers.

Since these are the first Mg/py/salen derivatives reported, the only viable models to compare the metrical data to are among themselves (2-5). Surprisingly, there were significant variations in the bond distances and angles noted based on the ligand employed, which can only be attributed to the rigidity of the ethylene diamine backbone (saloPh vs saloPh- Bu^t). In particular, the phenyl ring enforces a more rigorous OC-6 geometry around the Mg, but disorder was noted and is thought to be due to the strain of binding to the small Mg cation (0.86 Å, CN-6).⁵⁹ Figure 1e shows a diagram of some of the torsional angles discussed below to clarify the following discussion. The twist of the salen moiety is most evident in the dihedral angle between the N···N and the C-C of the phenyl ring (0.7 and 1.92° for 2; 23.6° for 3; 0° for 4; 1.3° for 5). The N-C-C-N torsion angle was found to be 0.75 and 2.13 ° for 2; 44.7° for 3; 0.18° for 4, and 2.45° for 5 demonstrating the rigidity induced by the phenyl backbone. The bend of the salen ligand around the metal was determined by measuring the para C atoms in the opposite rings and the metal $(C \cdots M \cdots C)$: 2 (14.3 and 15.4°); **3** (3.8°); **4** (11.5°); and **5** (41.7°). While the ethylene group twists more to accommodate the coordination of the metal, a phenyl backbone alternatively bends the salen ligand. The bound py molecules remain relatively linear with an average 177.3° angle (py-Mg-py); however, they can twist relative to each other (41 and 8.5° for 2; 0.4° for 3; 29.7° for 4). As can be noted by the two values for 2 there is a significant difference between the py twists of the two molecules present in the unit cell, possibly due to packing forces. The phenyl ring of the saloPh species was found to be bent from the Mg-N bonds by 9.29 and 9.77° for 2, 0.17° for 4, and 20.3° for 5. This is most likely a result of relieving the strain induced by the bend



Figure 5. Structure plot of (a) 4-tol and (b) 4a. The heavy-atom thermal ellipsoids are drawn at 30% level, with C atoms drawn as ball and stick and H atoms omitted for clarity.

of the rest of the saloPh ligand. Larger R1 values attributed to poor diffraction of the samples were observed for 3 and 5.

Elemental analyses on 2-5 were undertaken to verify purity (see Experimental Section). The data collected for 2-4 (the solvated Mg species) were not consistent with their solid-state structure. This was not unexpected, as solvated species tend to decompose inconsistently. The variance of these analyses being due to the solvent is comfirmed by the good agreement noted for 5. Attempts at using complexometric titrations to establish the purity of the bulk powder were not successful, as Mg is difficult to solubilize and complex. Therefore, TGA analyses were undertaken. From these experiments, weight losses were noted at ~140 °C for 2-4 but not for 5; therefore, the lack of a similar loss in the spectrum of 5 at low temperature indicates this weight change is associated with the loss of py. The next



Figure 6. Structure plot of **5**. The heavy-atom thermal ellipsoids are drawn at 30% level, with C atoms drawn as ball and stick and H atoms omitted for clarity.

thermal event noted for all of these compounds was observed above 300 °C. Weight losses stabilized after 550 °C for all samples except 3, which stabilized after 600 °C. Analyses of the residual powder indicated that periclase (MgO; PDF 00-045-0946) formed for all samples. The overall weight losses were similar to expected conversion percentages to periclase [cmpd (%calc; %exp): $2 \cdot py$ (7.0; 7.5); 3 (5.3 (+py); 5.0); 4 (5.0; 5.3); 5 (7.2; 7.5). This indicates that the majority of the bulk powders are consistent with the single-crystal structures with minor adjustments with solvent addition for 3.

¹H NMR spectra of 2–4 were collected in py- d_{5} , and selected resonances are listed in Table 2. Interpretation of the spectra is fairly straightforward with easily distinguishable py and saloR'-Bu^t resonances observed. The 8.70 ppm Ph–CH=N proton resonances noted for both 2 and 4 are therefore not a useful spectroscopic handle for identifying the various precursors. The –CH=N- resonances were expected to be the most distinguishing resonance; however, shifts of free ligands and the corresponding complexes were too similar to distinguish the individual compounds. In contrast, the –N–CH₂– resonances of the salo-Bu^t ligated complexes were found to shift 0.5 ppm upon complexation. The absence of these protons in the saloPh-Bu^t derivatives limits the impact of the observed shift.

The ¹H NMR spectrum of compound **5** was collected in both tol- d_8 and py- d_5 . The spectrum of the dinuclear **5** in toluene was extremely complicated, and no meaningful interpretation was made. The numerous peaks were attributed to the locked-out alkyls of the *t*-butyl groups, the potential monomer–dimer equilibrium, and/or partial bridging of the saloPh-Bu^t. The ¹³C NMR data were collected but due to low solubility additional information was not garnered. The spectrum of **5** in py- d_5 was identical to that of **4**, which demonstrates the simplicity with which **5** can coordinate py to render **4**.

Alternative analyses were investigated to aid in distinguishing the different ligands and metal binding noted for 2-5. UV-vis, FTIR, and Raman spectroscopy proved to be reliable methods for identifying the free ligand and Mg species. Select features of

Та	ble	2.	Select	Ana	lytical	Data	for	1 - 7
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	<i>.</i>		<i>i</i> 15	<i>.</i>	
cmpd no	NMR (py- d_5) -C(H)=N-	NMR (py- d_5) -C(H_2)-N-	UV-vis (nm^{-1})	FTIR (C=N) cm^{-1}	Raman (C=N) cm ⁻¹
H ₂ -saloPh	8.78		353	1613	1609
H_2 -salo- Bu^t	8.40	3.94	333	1626	1635
H ₂ -saloPh-Bu ^t	8.66		306	1615	1617
2	8.70		379	1611	1617
3	8.31	3.39	344, 375	1629	1617
4	8.70		354	1604	1642
5			353, 378	1614	1611
6	8.31	3.30	337, 420	1624	1629
7	8.55		354, 493	1594	1616

these spectra are tabulated in Table 2. The UV-vis spectra of the ligands and the Mg complexes (2-5) were collected in toluene. For 2-5, a broad peak between ~343 and ~419 nm was observed. The observed maxima are listed in Table 2, and the spectra are shown in Figure 7. These values are in agreement with reported ligand-to-metal charge-transfer transition bands of related metal-salen complexes.^{60,61}



Figure 7. UV-vis spectra of (a) Mg (2-5) and (b) Ca (6 and 7) derivatives.

For the free ligands, the FTIR stretch for the C==N was found at 1626 cm⁻¹ for H₂-salo-Bu^t and 1615 cm⁻¹ for H₂saloPh-Bu^t. Upon complexation to the metal, both the FTIR and Raman C==N stretch shifted by ~10 cm⁻¹. As desired, dual vibrational spectroscopy (FTIR and Raman) characterization successfully identifies each synthesized complex. This is a key feature for possible use of these compounds as fluid flow trackers in underground systems. Upon complexation to Mg, the FTIR imine stretches were shifted for 2–5 to 1611 (2), 1629 (3), 1604 (4), and 1614 (5) cm⁻¹. Similar shift trends were noted for the Raman spectral data for 2 (1617 cm⁻¹), 3 (1617 cm⁻¹), 4 (1642 cm⁻¹), and 5 (1611 cm⁻¹).

Ca Complexes. As the $Ca(R)_2$ precursors are not readily available, derivatization of H_2 -salen or H_2 -saloPh was

investigated using $[Ca(NR_2)_2]$ in toluene (eq 2). For both reactions, the parent metal-salen complex product rapidly precipitated upon mixing and remains insoluble in hot toluene. The salo-Bu^t and saloPh-Bu^t products were soluble in py, and upon crystallization by slow evaporation yielded the monomeric py-containing derivatives **6** (Figure 8) and 7 (Figure 9).



Figure 8. Structure plot of **6**. The heavy-atom thermal ellipsoids are drawn at 30% level, with C atoms drawn as ball and stick and H atoms omitted for clarity.

A CN-7 geometry around the metal occurs from the tetradentate salo-ligand (κ^4 -O,N,N',O') and the coordination of 3 py solvent molecules. The phenyl rings of the salo-Bu^t are planar but at the cost of a twisted ethyl group on the diamine (27.9°). In contrast, the rigidity induced by the phenyl ring of the saloPh-Bu^t causes a substantial bend in the rings of the salo moiety.

The metrical data of 6 and 7 (Table 1) were not as influenced by the ligands as noted for 2-5. The majority of the bond angles are identical with the major difference noted at the O-M-O angle. This may be due to the electron donation and steric bulk of the three bound py ligands. The trans py solvent molecules were found to be only slightly twisted, with an



Figure 9. Structure plot of 7. The heavy-atom thermal ellipsoids are drawn at 30% level, with C atoms drawn as ball and stick and H atoms omitted for clarity.

average 2.7° torsion angle. The twist of the salo moiety around the N···N and C–C bonds (see Figure 1e) are 27.9° for 6 but 0.5° for 7. However, the phenyl ring of the diamine and the phenoxy rings are bent away from each other. The N–C–C–N dihedral angle was found to be 56.5 and 2.13° for 6 but only 0.88° for 7, showing the induced rigidity of the phenyl backbone. Further, as noted above, the twist that the backbone endures forces the phenyl salen species to bend significantly: 18.7° for 6 versus 46.0° for 7. Again, because of this bend the phenyl ring of the saloPh derivative 7 was angled away from the Ca–N bonds by 39.1°.

Elemental analyses on 6 and 7 were also measured and, in contrast to 2-5, were found to be in good agreement with the solid-state structures. For 7, this required the loss of a py ligand to garner acceptable percentages. TGA analyses of these compounds revealed weight losses initiated at ~140 °C, which

were associated with the loss of the py solvent molecules. The next thermal event occurred greater than 270 $^{\circ}$ C and was finalized by 750 $^{\circ}$ C. Powder X-ray diffraction (PXRD) analyses of the residual powder revealed lime (CaO; PDF 00-037-1497) had formed for both samples.

Solution ¹H NMR spectra of **6** and 7 were found to be in agreement with the solid-state structure, with one set of resonances observed for the various components. Similar Ph-HC=N shifts of 8.31 ppm for 6 and 8.55 ppm for 7 were observed. Comparison of these spectra with 2-4 revealed a similar shift for 6 and 3 that limits using this distinguishing resonance. Because of the success of the UV-vis, FTIR, and Raman spectral differentiation noted for the free ligands and their Mg complexes, these techniques were utilized similarly for the Ca complexes. Broad bands, similar to 2-5, were also observed in the UV-vis spectra of 6 and 7 (see Figure 7 and Table 2). The broad peak between \sim 338 and \sim 419 nm are again attributed to ligand-to-metal charge-transfer transition bands.^{60,61} As for the FTIR spectra, upon complexation to Ca the H₂-salo-Bu^t imine stretch was shifted from 1626 to 1624 cm^{-1} for 6, and the H₂-saloPh-Bu^t stretch shifted from 1615 to 1594 cm⁻¹ for 7. Similar shifts were noted for the Raman spectral data: 1635 cm⁻¹ for H₂-salo-Bu^t versus 1629 cm⁻¹ for **6** and 1617 cm⁻¹ for H₂-saloPh-Bu^t versus 1616 cm⁻¹ for 7.

Modeling. As an initial step in the development of molecular simulation methodologies to predict the behavior of these compounds in underground environments, DFT calculations of gas-phase clusters of 2-7 were used to compare the effect of ligand chemistry on structural properties. Such simulations can be used to assist in identifying the solution behavior of these compounds in oil (hydrophobic, organic), water (hydrophilic), or a mixture of the two. Subsurface behavior can also be simulated in this manner. The models were developed and compared to the crystal structures (see Table 1). Overall, a comparison of the model's angles and



Figure 10. DFT-optimized structures of the Mg-L complexes of (a) "Mg(salen)(py)2", (b) 2, (c) 3, (d) 4, and (e) 5.

distances to those of the single-crystal structure were found to be consistent.

a. Magnesium. The DFT-optimized structures of the various Mg-salo-R complexes are shown in Figure 10a-e. In the structural model of the salen ligands, there is significant twisting about the C-N-N-C dihedral of the ethylenediamine group due to the strain imposed by the OC-6 coordinated Mg cation. In fact, the N-C-C-N dihedral angles are ~49° for the salen of 3, compared with dihedral angles $\sim 0^{\circ}$ for the saloPh compounds (2, 4, and 5). The general trend of the dihedral angles is consistent with the single-crystal structures noted previously with 2, 4, and 5 being nearly 0°; however, the large 49° twist noted for the model is more than twice that seen in the structure of 3.

Another significant difference between the calculated Mg-(salen) and 2 is the orientation of two axially bound py ligands, resulting in what initially appears to be C_2 rotational symmetry; however, the py ligands of 2 are perpendicular to each other, which disrupts the C_2 symmetry. A twist in the py orientation was noted for 2–4 but was not as much as the model indicated; the largest twist noted was for 4 at 29.7°. Furthermore, the three phenyl rings of 2 (Figure 10b) are not planar where the two rings along the x-axis are tilted upward by $\sim 8^{\circ}$ and the central phenyl ring along the y-axis is tilted downward by $\sim 8^{\circ}$. This maximizes the short-range interactions with the two py ligands. Introduction of the Bu^t groups onto the rings introduces an off-plane tilt by $\sim 6^{\circ}$ (Figure 10d) for 4. The saloPh-Bu^t ligands in compound 5 show significant nonplanarity, likely due to the steric hindrance of the two ligands in such close proximity. Angles centered on the Mg atoms in 5 are also reduced compared to the monomer 4 (Table 1). This general trend of salo ligand bends were noted in the experimental data as well.

b. Calcium. Optimized structures of 6 and 7 (Figure 11) were found to be similar to the Mg species, but due to the larger Ca cation,⁴⁷ a third py ligand located in the equatorial plane binds to Ca forming a CN-7 geometry. The ethylenediamine group in 6 is twisted with a N-C-C-N dihedral angle of 59°, which is significantly larger than noted for the Mg system (vide infra). This angle is larger than noted for the experimentally derived structures, but the general trends are again consistent. Additionally, the four coordinating donor atoms of the salo backbone were found to be significantly deviated from planarity. The dihedral angles involving the metal atom and two coordinated atoms (e.g., N-M-O-C) range from 34° to 46° for 6 and 7. In contrast, the same angles observed for 2–4 range from 3° to 9°.

Fluid Flow Parameters. Critical for practical use, these salen-based tracers must survive the high temperatures and pressures typically noted for deep-well conditions, easily loaded into, and freely elute from, the carrier proppants, and flow to the surface without binding to underground strata. Therefore, an initial evaluation of 2–7 for use as potential underground tracers was undertaken, and the properties determined are discussed according to (i) thermal/pressure stability, (ii) interaction with surfaces (SiO₂ columns), and (iii) elution data from the proppant. The conditions associated with a deep well (or "bottom-hole conditions" at 1800 m) will be considered as follows: 80 °C, 6000 psi pressure in a silica environment to simulate the rock formations underground.^{62–66} Because of variations in the contents, location, and well composition, these values vary considerably; however,



Figure 11. DFT-optimized structures of the Ca-salo complexes (a) 6 and (b) 7.

these conservative parameters are considered at the high end of the bottom-hole conditions.

I. Thermal/Pressure Stability. To test the stability of the precursor, several experiments with "model oils" were conducted on 3-7. The thermal robustness of these compounds in toluene at reflux temperatures was undertaken. Toluene was selected due to its boiling point, similarity to some oil components, and the fact that subsequent computational modeling uses toluene as a model oil as well. All samples were dissolved in toluene, heated for 12 h, and then dried. FTIR data indicated that each sample was found to survive intact.

Next, the samples were dissolved in toluene (30 mL), placed into a Teflon-lined Parr bomb, and heated to 120 °C for 12 h under SOLVO conditions. At these conditions, pressures as high as 1450 psi were calculated to exist. Extraction of the compounds after this reaction indicated that 5-7 had maintained their original FTIR spectra (vide supra). The Mg derivatives (2-4) were slightly altered, which was assumed to be due to loss of coordinated solvent, which was confirmed by the similarity of the FTIR spectra of a series of toluenegenerated Mg-saloR-Bu^t powders and the material recovered from the Parr bomb (see Supporting Information, Figure S1). In comparison to the Mg species, the Ca derivatives (6 and 7)must have a stronger interaction with the py that prevents this disassociation. This is borne out by the bond distances reported in the structural literature (i.e., Ca-N (range 2.495-2.641 Å vs Mg–N (range 2.117–2.376 Å))⁶⁷ when the cation variations (Mg, CN-6, 0.71 Å; Ca CN-6, ;1.14 Å)⁵⁹ are taken into account.

Evaluation at higher temperatures were sought, so the samples of 3-6 were individually placed into a Parr bomb containing 25 mL of dodecane. Dodecane was selected due to its longer hydrocarbon chain length and higher boiling point. The sealed Parr bomb was placed into a box furnace at 180 °C

for 24 h, with an expected pressure of 2220 psi. After it cooled to room temperature, the samples were evaluated by FTIR for their distinguishing features (vide supra). On the basis of these data, it was evident that none of the samples survived the process (Supporting Information Figure S2). The soluble fraction of 3 and 4 were concentrated, and the crystals isolated from the reaction mixture proved to be the original H2-saloR'-Bu^t ligand; the insoluble fraction was amorphous, but heat treating at 400 °C indicated magnesium oxide (PDF 01-076-9192) or periclase (01-071-6488), respectively, had been isolated. The products isolated from 6 and 7 possessed calcium oxide (01-077-7243) along with several other Ca species. While these data indicated that the compounds would not survive at these high temperatures and pressures, it is of note that these conditions exceed what would be expected or required for a bottom-hole.

ii. Retention. The need for these metal-ligand complexes to remain soluble in the product fluids is obvious, as premature deposition onto underground rock formations would alter both qualitative and quantitative results. Attempts to determine the mobility and potential deposition of these molecules in underground caverns were initially investigated using columns of sand (SiO_2) . The preweighed samples were dissolved in toluene, a column of packed sand was saturated with toluene, and the samples were loaded onto the column. The sample was run through the column at a continuous flow rate of 0.065 mL sec^{-1} , then flushed with excess toluene to ensure full elution. The sample was then collected and dried. For three of the four samples studied (2, 3, and 4) an ~100% yield by weight recovery was obtained. A reduced recovery of 74% yield by weight was noted for 5 and is attributed to partial deposition on the column's surface. Follow-on molecular simulations will determine the extent of interaction of similar compounds with clay mineral phases. Refinement of these samples for the various underground minerals (silica, kaolinite, and montmorillonite) have been successfully modeled;⁶⁸ however, experimental verification is necessary to establish the proper constituents of the precursors for the different regions the wells may exist in.

iii. Elution Data. As mentioned previously, for the prepared metal-salen ligand complexes to be useful in tracking fluid flows the infused complexes must elute from the underground proppants upon exposure to the produced fluid and remain soluble until they are analyzed above-ground. As the fluid flowing from underground is typically a mixture of hydro-carbons (i.e., organic product) and water, when eluted they will partition into either the organic or aqueous phases. Laboratory-scaled elution testing equipment was used to simulate the "real world" performances of experimental samples by flowing the desired fluid over a proppant pack and measuring the amount of complex found in sample aliquots over time (Figure S3). There are at least three key points to keep in mind when evaluating these samples.

First, the amount of complex released into the produced fluid is expected to decrease over time, as the concentration of infused complex decreases within the proppant. Elution experiments were conducted at a constant flow rate, and aliquots were taken as a function of time. The eluted fluid volume is converted to pore volumes for elution profile analysis. This pore volume concept is very similar to the established liquid hourly space velocity (LHSV) concept used in liquid flow catalytic studies. For this system (vide infra), the level of Mg found in the aliquots after 4, 20, and ~40 pore volumes of liquid passed over the Mg-salen loaded proppant package was analyzed.

Second, the testing solvent can be either an aqueous salt solution that simulates a formation brine or a long-chain hydrocarbon (such as Isopar L) to mimic the organic products. Typically, it is much easier to analyze samples in aqueous media, as inductively coupled plasma techniques can be used to accurately measure the metal concentration. However, for this effort we were interested in evaluating the Mg-salen concentrations in hydrocarbons. As such, a procedure using AAS (described in the Experimental Section) was developed to analyze the low Mg levels found in the organic solvent.

Third, we note that it is possible to put a polymeric coating on proppant particles to retard the elution rate of the Mg-salen species from the package and thus extend the operating lifetime of the proppant package. However, our goal in this study was to experimentally demonstrate the concept that the M-salen (M =Mg, Ca) complexes developed could function as taggants for monitoring underground fluid flow. For expediency, we were interested in the *accelerated* elution of these compounds during the lab testing; thus, polymeric coatings were not put on the proppant after it was loaded.

For this report, our initial analyses were undertaken on a proppant pack infused with 4, utilizing the equipment shown in Figure S3. As expected, the level of eluted Mg-salen complex decreased markedly from the initial phase of the testing (176 ppb, aliquot taken after four pore volumes had been collected) to the intermediate sampling taken at the 20 pore volume mark (29 ppb), to the latter stages of testing at the ~40 pore volume mark (9 ppb). This decline in measured Mg levels is shown graphically in Figure 12, and these results indicate that these



Figure 12. Concentration of Mg from 4 in eluted Isopar L as a function of equivalent pore volumes eluted.

salen-metal species loaded into proppants meet the preliminary requirement that they gradually elute from the proppant package over time. Further ongoing studies are focused on evaluating long-term elution performances using both aqueous and hydrocarbon fluids. These results will be published, when appropriate, in more industrially focused journals.

CONCLUSION AND SUMMARY

A series of pyridine-solvated alkaline-earth salen derivatives (Mg: 2–4a; Ca: 6 and 7) have been isolated and structurally characterized as monomeric κ^4 -(O,N,N',O')saloR-R' species. Additionally, a solvate-free Mg complex was isolated as the

dinculear complex 5 adopting a κ^3 -(O,N,N'), μ -(O') binding. For each of the solvates, the salen moiety was found to adopt a tetradentate (κ^4 -(O,N,N',O')) binding mode. For the smaller congener Mg, one or two py molecules were bound to the metal forming CN-5 or CN-6, respectively, whereas the larger Ca ion binds three py molecules to fill its CN-7 coordination sphere. The twists of the salen ligands are less dependent on the metal and more on the backbone of the salen ligand: salo (twist 23.6° to 27.9°) versus saloPh (twist 0 to 1.3°). Twisting of the ethylene backbone allows the rest of the salo ligand to remain relatively planar, whereas the saloPh derivatives have the phenoxy rings significantly bent away from the central plane to relieve strain. These trends were also observed in the complementary DFT calculations. The high agreement between the DFT calculations and experimental results enables the development of meaningful models of the subterranean fluid flow. Eventually, atomic charges and geometric properties will be used in large-scale molecular simulations to investigate the behavior of these compounds in oil and/or aqueous solutions and to understand their adsorption characteristics onto mineral surfaces found underground. Elution tests using 4 loaded into a proppant and Isopar L as simulant for underground oil reservoir revealed the desired gradual release of 4 into the fluid flow, thus verifying the potential use of such compounds as taggants. Additional work, exploring this family of compounds and other derivatives⁶⁹ as a means to monitor underground fluid flow, is underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01350.

Atomic coordinates, data collection parameters, and CHELPG charges for 1-7 (PDF)

Accession Codes

CCDC 1547258–1547264 and 1571279 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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