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Manganese-containing ionic liquids: synthesis, crystal structures and electrodeposition of manganese films and nanoparticles[†]

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Manganese(II)-containing ionic liquids were synthesized, in which the manganese atoms are coordinated by glymes (diglyme, triglyme, tetraglyme), pyridine-*N*-oxide, dimethylsulfoxide or *N*-alkylimidazoles (*N*-methylimidazole, *N*-butylimidazole and *N*-hexylimidazole). As anion, bis(trifluoromethanesulfonyl)imide (bistriflimide, Tf₂N[−]), trifluoromethanesulfonate (triflate, OTf[−]) or methanesulfonate (mesylate, OMs[−]) were used. The compounds were characterized by CHN analysis, FTIR, DSC and single-crystal X-ray diffraction measurements. All manganese atoms were six-coordinate. It was found that the glyme-type ligands were replaced by atmospheric water upon leaving the crystals open to the air for several days. The crystal structures of seven compounds were described in detail and the compounds with the lowest melting temperatures were tested as electrolytes for the electrodeposition of manganese (thin) films. An irreversible reduction wave from Mn(II) to Mn(0) and granular manganese deposits were observed for all compounds, except for liquid manganese salts with *N*-alkylimidazole ligands and bistriflimide anions, where the electrochemical formation of manganese nanoparticles was observed instead of the deposition of a manganese layer. However, for compounds with the same cation but with a triflate or methanesulfonate anion, manganese metal deposits were obtained, indicating that the nature of the anion has an important effect on the electrochemical properties of liquid metal salts.

1 Introduction

Ionic liquids are compounds that usually consist of bulky organic cations and large, mostly non-coordinating anions and that are liquid at temperatures below 100 °C.^{1–4} Since they consist only of ions, they have interesting properties such as an intrinsic ionic conductivity and a negligible vapor pressure. They are interesting for electrochemical applications since most of them have a wide liquidus range and a broad electrochemical window, allowing metals to be deposited that cannot be deposited from water.^{5–7} Unfortunately, many common metal salts have a low solubility in ionic liquids with weakly coordinating anions. Also, due to their high viscosity, current densities of electrochemical processes in ionic liquids tend to be lower than in water.^{8,9} To counteract these drawbacks, a new class of ionic liquids called Liquid Metal

Salts (LMS) was developed.¹⁰ In these ionic compounds, a metal cation is coordinated by neutral ligands and combined with a non-coordinating anion to form an ionic liquid of which the metal is an inherent part of the molecular structure. This circumvents any solubility issues. Since the cathodic degradation of the liquid metal salt is the desired deposition of the metal, very high current densities can be achieved. Several examples of these kind of compounds can be found in the literature,^{11–14} including electrodeposition from liquid metal salts.^{15–22}

Current densities up to −25 A dm^{−2} could be obtained for copper deposition from the copper(I) LMS [Cu(MeCN)₄][Tf₂N].^{10,23,24} High current density depositions were also described for silver(I),^{25–29} palladium(II)³⁰, zinc(II)³¹ and lithium(I).³² It was found that from nickel(II) containing LMS, nickel nanoparticles could be synthesized electrochemically at 100 % selectivity when imidazole ligands were used with a sufficiently large side chain on the imidazole ring.³³ Recently, we also described promising results on the use of liquid metal salts as electrolytes for redox flow batteries.³⁴

In this paper, the concept of liquid metal salts is further expanded to manganese(II)-containing LMS. Due to its negative standard redox potential ($E^0(\text{Mn}^{2+}/\text{Mn}) = -1.18 \text{ V}_{\text{SHE}}$), the

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stability region of manganese metal is outside the limit of the electrochemical window of water, meaning it is not possible to electrodeposit manganese from aqueous solutions without hydrogen evolution.^{35,36} As an alternative to aqueous electrolytes, the high temperature deposition of Al-Mn³⁷ and Zn-Al-Mn alloys from molten salts for corrosion protection layers has been described before^{38–40} and Zn-Mn alloys have been electrodeposited from acidic aqueous solutions containing a variety of additives.^{41–43} Manganese alloys have also been deposited from ionic liquids, such as Al-Mn alloys from [EMIM][Cl],⁴⁴ (EMIM = 1-ethyl-3-methylimidazolium) Zn-Mn alloys from [EMIM][Tf₂N],⁴⁵ Zn-Mn alloys from [Bu₃MeN][Tf₂N],⁴⁶ (Bu₃MeN = tributylmethylammonium) and Cu-Mn alloys from [BMP][Tf₂N] (BMP = 1-butyl-1-methylpyrrolidinium).⁴⁷

Electrodeposition of manganese metal without other alloying metals has not been studied extensively. To the best of our knowledge, the only reports on the deposition of manganese from ionic liquids have been published by Sun *et al.* who used [BMP][Tf₂N]^{48,49} and [BMP][DCA] (DCA = dicyanamide).⁵⁰ Since no commercially available manganese salts are soluble in those ionic liquids, these authors introduced Mn(II) into the liquid by anodic dissolution of a metallic manganese electrode. Their CVs show cathodic deposition of manganese and several small stripping peaks, but in general the deposition of manganese is irreversible.⁴⁸ The irreversibility was ascribed to the kinetic hindrance for the formation of a Mn(Tf₂N)₂ species, a process that might be too slow to respond to the scan rate of 50 mVs^{−1} and that was also seen for deposition of other metals.^{51,52} The manganese deposits obtained by Sun *et al.* were composed of spherical structures with a diameter of 400 nm. Each spherical structure consisted of sub-grains that were a few nanometers in size.⁴⁹ Controlled-potential coulometry experiments showed a current efficiency approaching 100% for the deposition of manganese.

We describe several new manganese(II)-containing liquid metal salts in which the manganese atom is coordinated by different oxygen or nitrogen donor atoms in the ligands. As ligands, bis(2-methoxyethyl)ether (diglyme, G₂), triethylene glycol dimethyl ether (triglyme, G₃), tetraethylene glycol dimethyl ether (tetraglyme, G₄), pyridine-*N*-oxide (py-O), dimethylsulfoxide (DMSO), *N*-methylimidazole (MeIm), *N*-butylimidazole and *N*-hexylimidazole (HeIm) are used. Several crystal structures are reported as well as their chemical and electrochemical properties. An overview of all the used ligands and anions used in the synthesis of manganese(II) liquid metal salts can be found in Figure 1.

2 Experimental

2.1 General

All ligands were purchased from Sigma-Aldrich (Diegem, Belgium) or Acros Chemicals (Geel, Belgium), with the exception of *N*-hexylimidazole which was ordered from IoLiTec (Heilbronn, Germany). Also bistriflimic acid (80 % aqueous solution), trifluoromethanesulfonic acid and methanesulfonic acid were

Fig. 1 Chemical structures of all the used ligands and anions.

obtained from IoLiTec. All products were used without further purification. Melting points were determined on a Mettler-Toledo DSC 1 instrument, using a heating rate of 10 °C min^{−1} and under a helium atmosphere. Elemental analyses (CHN) were carried out on a CE Instruments EA-1110 elemental analyzer. Infrared spectra were recorded using an attenuated total reflectance (ATR) technique on a Bruker Vertex 70 FTIR spectrometer with a Platinum ATR extension with a resolution of 4 cm^{−1}. Peak assignment was based on literature data.^{53–55} Thermogravimetric analysis was performed on a TA Instruments TGA Q500 under nitrogen-atmosphere at a heating rate of 5 °C min^{−1}. Viscosities were measured using an Anton Paar LOVIS 2000 ME Microviscometer. Since the use of this device requires careful filling of a capillary, viscosity measurements could only be performed on the compounds that were liquid at room temperature. Grazing incidence X-ray diffraction (XRD) was performed on a Seifert 3003 T/T diffractometer, using Cu K_α radiation with $\lambda = 1.54056 \text{ \AA}$ and an incidence angle of 1°. Characterization of the nanoparticles was performed on a CM 200 FEG Custom transmission electron microscope, equipped with a GATAN magnetic imaging filter.

2.2 Electrochemistry

Platinum-coated silicon wafers (Pt layer of 100 nm) were used as working electrodes for electrodeposition. All electrodes were washed with HCl and rinsed with demineralized water and acetone and dried. All electrochemical experiments were conducted in a glovebox (with H₂O and O₂ concentrations below 1 ppm). Cyclic voltammograms were measured using an Autolab PGSTAT 302N electrochemical interface controlled by a computer with GPES software in an unstirred solution. All potential values are measured versus a reference electrode consisting of a platinum wire immersed in an equimolar ferrocene/ferrocenium solution in [BMP][Tf₂N]. As counter electrode, a manganese plate was used. Unless stated otherwise,

all cyclic voltammograms were measured starting at open circuit potential (OCP) and scanning first in the cathodic direction.

2.3 Crystallography

Single crystals of a quality suitable for single crystal X-ray diffraction were obtained by melt crystallization, crystallization from ethanol or acetone for the following compounds: $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{G}_2)_1][\text{OTf}]_2$ and $[\text{Mn}(\text{MeIm})_6][\text{Tf}_2\text{N}]_2$. The crystals were mounted on a nylon loop in the N_2 (100(2) K) stream of an Oxford Cryostream 700 using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied using CrysAlisPro (Agilent Technologies, Yarnton, UK, 2011). Structures were solved using direct methods and refinement was performed by the full-matrix least-squares procedure in SHELXL⁵⁶ using the graphical interface OLEX2.⁵⁷ Images of the crystal structures were also obtained from this program. All hydrogen atoms were placed in calculated positions and refined using a riding model. CCDC 1511760-1511766 contain all crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4 Synthesis

2.4.1 $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$

A suspension of manganese(II) oxide (10.00 g, 141 mmol) in a solution of hydrogen bistriflimide (80 wt% aqueous solution) (99.1 g, 282 mmol) in H_2O (50 mL) was stirred for 20 hours at 85 °C after which the remaining solids were filtered off. The excess of solvent was removed on a rotary evaporator and the product was dried overnight at room temperature on a vacuum line, yielding a white solid product at room temperature (97.91 g, 96%). TGA analysis showed the loss of six water ligands at elevated temperatures. There is also a near perfect match between experimental and calculated CHN analysis data if six water molecules are considered in the calculation. Melting point: 94 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3493 (H_2O), 1625, 1326, 1195 (CF_3), 1122 (SO_2), 1041 (SNS), 794, 771, 742 (CF_3), 631 (SNS), 611 (SO_2), 587, 571 (CF_3), 508. CHN found (calculated for $\text{C}_4\text{H}_{12}\text{F}_{12}\text{MnN}_2\text{O}_{14}\text{S}_4$): C 6.64 (6.86) %, H 1.67 (1.73) %, N 3.87 (3.80) %.

2.4.2 $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$

A solution of $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ (5.00 g, 6.50 mmol) and diglyme (1.85 g, 13.8 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white glassy solid at room temperature (6.31 g, 98%). No melting point was observed by DSC-measurements and the compound was fluid at 50 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 2957 (CH), 1459, 1353, 1322, 1228, 1176 (CF_3), 1131 (SO_2), 1082, 1049 (SNS), 939, 862, 789, 740 (CF_3), 652, 615 (SO_2), 598, 569 (CF_3), 507, 406. CHN found (calculated for $\text{C}_{16}\text{H}_{28}\text{F}_{12}\text{MnN}_2\text{O}_{14}\text{S}_4 \cdot 6\text{H}_2\text{O}$): C 19.28 (19.37) %, H 4.02 (4.06) %, N 3.07 (2.82) %.

2.4.3 $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$

A solution of $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ (5.00 g, 6.50 mmol) and triglyme (1.23 g, 6.90 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white glassy solid at room temperature (5.94 g, 99%). Glass transition: -63 °C. No melting point was observed by DSC measurements and the compound was fluid at 50 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 2953 (H_2O), 2898 (CH), 1474 (CH), 1345 (SO_2), 1318, 1184 (CF_3), 1126 (CF_3), 1050 (SNS), 953, 879 (CH), 851 (CH), 789 (CS), 746, 654 (SNS), 596, 571 (CF_3), 508 (CF_3), 406 (SO_2). CHN found (calculated for $\text{C}_{12}\text{H}_{18}\text{F}_{12}\text{MnN}_2\text{O}_{14}\text{S}_4 \cdot 6\text{H}_2\text{O}$): C 16.01 (15.99) %, H 3.44 (3.35) %, N 3.25 (3.11) %.

2.4.4 $[\text{Mn}(\text{G}_4)_1][\text{Tf}_2\text{N}]_2$

A solution of $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ (5.00 g, 6.50 mmol) and tetraglyme (1.55 g, 6.90 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white glassy solid (5.28 g, 97%). FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3451 (H_2O), 2959 (CH), 1463 (CH), 1353 (SO_2), 1323 (SO_2), 1179 (CF_3), 1131 (CF_3), 1086 (SNS), 1049 (SNS), 1018, 989, 953, 941, 853 (CH), 837, 794 (CS), 741 (CF_3), 610 (SO_2), 569 (CF_3), 510 (CF_3). CHN found (calculated for $\text{C}_{14}\text{H}_{23}\text{F}_{12}\text{MnN}_2\text{O}_{13}\text{S}_4$): C 20.13 (20.05) %, H 3.03 (2.76) %, N 3.47 (3.34) %.

2.4.5 $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$

A solution of $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ (5.00 g, 6.50 mmol) and dimethylsulfoxide (3.24 g, 41.4 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white solid (6.97 g, 99%). Melting point: 51 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3109 (H_2O), 2929 (CH), 1417, 1343 (SO_2), 1332 (SO_2), 1315, 1230 (CF_3), 1180 (CF_3), 1133 (CF_3), 1055 (SNS), 998, 953, 930, 788 (CS), 740 (CF_3), 715, 652 (SNS), 600 (SO_2), 570 (CF_3), 507 (CF_3), 414 (SO_2). CHN found (calculated for $\text{C}_{16}\text{H}_{36}\text{F}_{12}\text{MnN}_2\text{O}_{14}\text{S}_{10}$): C 17.72 (17.50) %, H 3.35 (3.55) %, N 2.52 (2.58) %.

2.4.6 $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$

A solution of $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ (5.00 g, 6.50 mmol) and pyridine-*N*-oxide (3.94 g, 41.4 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a bright yellow solid (7.55 g, 98%). Melting point: 92 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3124 (CH), 1471 (ring), 1351, 1331, 1227 (NO), 1174 (NO), 1132 (SO_2), 1052 (SNS), 1022 (ring), 834 (NO), 765 (CH), 740 (CF_3), 672, 610 (SO_2), 569 (CF_3), 557, 512, 462. CHN found (calculated for $\text{C}_{34}\text{H}_{30}\text{F}_{12}\text{MnN}_8\text{O}_{14}\text{S}_4$): C 34.21 (34.44) %, H 2.56 (2.55) %, N 9.16 (9.45) %.

2.4.7 [Mn(MeIm)₆][Tf₂N]₂

A solution of Mn(Tf₂N)₂·6H₂O (5.00 g, 6.50 mmol) and *N*-methylimidazole (3.41 g, 41.4 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white solid (7.55 g, 100%). Melting point: 110 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 1531 (ring), 1348 (SO₂), 1173, 1138 (CH₃), 1086 (CH), 1051 (SNS), 933 (ring), 829, 745 (CH), 660 (SNS), 609 (SO₂), 568 (CF₃), 512 (CF₃). CHN found (calculated for C₂₈H₃₆F₁₂MnN₁₄O₈S₄·3H₂O): C 28.94 (30.36) %, H 3.38 (3.64) %, N 16.66 (16.87) %.

2.4.8 [Mn(BuIm)₆][Tf₂N]₂

A solution of Mn(Tf₂N)₂·6H₂O (5.00 g, 6.50 mmol) and *N*-butylimidazole (5.15 g, 41.4 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a colorless liquid at room temperature 8.49 g, 96%). No melting point nor glass transition could be observed by DSC measurements. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3129 (CH), 2962 (CH), 2936 (CH), 2877 (CH), 1514 (ring), 1462, 1349, 1332, 1228 (CF₃), 1180 (CF₃), 1136 (SO₂), 1108, 1087, 1055 (SNS), 933, 827, 787, 739 (CF₃), 662, 600 (SO₂), 570 (CF₃), 512. CHN found (calculated for C₄₆H₇₂F₁₂MnN₁₄O₈S₄): C 40.87 (40.61) %, H 5.40 (5.33) %, N 14.22 (14.42) %.

2.4.9 [Mn(HeIm)₆][Tf₂N]₂

A solution of Mn(Tf₂N)₂·6H₂O (5.00 g, 6.50 mmol) and *N*-hexylimidazole (6.32 g, 41.4 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a colorless liquid at room temperature (9.83 g, 98%). No melting point nor glass transition was observed by DSC measurements. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3129 (CH), 2957 (CH), 2932 (CH), 2861 (CH), 1595, 1514 (ring), 1457, 1350, 1332, 1284, 1228 (CF₃), 1181 (CF₃), 1137 (SO₂), 1108, 1086, 1056 (SNS), 933, 827, 787, 760, 739 (CF₃), 662, 615, 600 (SO₂), 570 (CF₃), 512. CHN found (calculated for C₅₈H₉₆F₁₂MnN₁₄O₈S₄): C 45.51 (45.57) %, H 6.39 (6.33) %, N 12.72 (12.83) %.

2.4.10 Mn(OTf)₂·6H₂O

A solution of manganese(II) oxide (5.00 g, 70.5 mmol) and triflic acid (21.15 g, 0.141 mol) in water (50 mL) was stirred for 20 hours at 85 °C after which the remaining solids were filtered off. The excess of solvent was removed on a rotary evaporator and the product was dried overnight at room temperature at a vacuum line, yielding a white solid at room temperature (29.91 g, 92%). Melting point: 86 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3458 (H₂O), 1630, 1227 (CF₃), 1186 (CF₃), 1030, 625 (SO₃), 588, 521, 508 (CF₃), 472, 459, 437, 420 (SO₃). CHN found (calculated for C₂F₆MnO₆S₂·6H₂O): C 5.37 (5.21) %, H 2.62 (2.62) %, N 0.00 (0.00) %.

2.4.11 [Mn(G₂)₁][OTf]₂

A solution of Mn(OTf)₂·6H₂O (5.00 g, 10.8 mmol) and diglyme (1.45 g, 13.8 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white glassy solid (7.63 g, 99%). Melting point: 189 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 1317, 1176 (CF₃), 1029, 737, 627 (SO₃), 519. CHN found (calculated for C₈H₁₄F₆MnO₉S₂·4H₂O): C 17.41 (17.18) %, H 4.20 (3.97) %, N 0.00 (0.00) %.

2.4.12 [Mn(HeIm)₆][OTf]₂

A solution of Mn(OTf)₂·6H₂O (5.00 g, 10.8 mmol) and *N*-hexylimidazole (9.90 g, 65.1 mmol) in acetonitrile (25 mL) was stirred for 60 min at room temperature. The excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white solid (13.27 g, 97%). Melting point: 87 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 2929 (CH), 2360, 1520 (ring), 1507 (ring), 1457 (ring), 1264 (NH), 1238 (CF₃), 1154 (CF₃), 1088, 1029, 933 (ring), 828, 762, 663, 635, 571 (CF₃), 515 (CF₃), 419 (SO₂). CHN found (calculated for C₅₆H₉₆F₆MnN₁₂O₆S₂): C 52.96 (53.11) %, H 7.38 (7.64) %, N 13.33 (13.27) %.

2.4.13 [Mn(H₂O)₆][OMs]₂

A solution of manganese(II) oxide (5.00 g, 70.5 mmol) and methanesulfonic acid (13.55 g, 0.141 mol) in water (50 mL) was stirred for 20 hours at 85 °C after which the remaining solids were filtered off. The excess of solvent was removed on a rotary evaporator and the product was dried overnight at room temperature on a vacuum line, yielding a white solid at room temperature (22.16 g, 89%). Melting point: 209 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3464, 1168, 1044, 782, 509. CHN found (calculated for C₂H₆MnO₆S₂·6H₂O): C 6.72 (6.80) %, H 5.05 (5.14) %, N 0.00 (0.00) %.

2.4.14 [Mn(HeIm)₆][OMs]₂

A solution of Mn(OMs)₂·6H₂O (5.00 g, 14.2 mmol) and *N*-hexylimidazole (12.9 g, 84.9 mmol) in water (25 mL) since the starting product is not soluble in acetonitrile, and the mixture was stirred for 60 min at room temperature. The excess of water was removed on a rotary evaporator and the product was dried overnight on a vacuum line, yielding a white solid (16.29 g, 99%). Melting point: 106 °C. FTIR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 2925 (CH), 1540 (ring), 1520 (ring), 1457 (ring), 1229 (NH), 1180 (CF₃), 1111, 1089, 1045, 934 (ring), 825, 764, 664, 548, 531, 518, 419 (SO₃). CHN found (calculated for C₅₆H₁₀₂MnN₁₂O₆S₂): C 57.99 (58.06) %, H 8.92 (8.87) %, N 14.44 (14.51) %.

3 Results and Discussion**3.1 Synthesis**

Mn(Tf₂N)₂·6H₂O, Mn(OTf)₂·6H₂O and Mn(OMs)₂·6H₂O were prepared by dissolving MnO in bistriflimic acid, trifluoromethanesulfonic acid and methanesulfonic acid, respectively. The excess of solvent and the water formed by the neutralization reaction were removed *in vacuo* and the resulting

Table 1 Overview of the synthesized compounds and their melting points.

Compound	Melting point (°C)
$[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$	< 50
$[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$	< 50
$[\text{Mn}(\text{G}_4)_1][\text{Tf}_2\text{N}]_2$	> 200
$[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$	51
$[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$	92
$[\text{Mn}(\text{MeIm})_6][\text{Tf}_2\text{N}]_2$	110
$[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$	< R.T.
$[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$	< R.T.
$[\text{Mn}(\text{G}_2)_1][\text{OTf}]_2$	189
$[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$	87
$[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$	106

product was dried overnight on a vacuum line. For the synthesis of the manganese(II)-containing ionic liquids, a stoichiometric amount of the ligand is added to this starting product.

Thermogravimetric analysis (TGA) traces of all compounds are presented in Figure 2. Most compounds, except for those with diglyme and triglyme ligands, are stable up to about 100 °C, after which they start losing mass. It is probable that the hygroscopicity of the diglyme and triglyme compounds causes loss of atmospheric water at lower temperatures. It is worth mentioning that all liquid manganese salts with a bistriflimide anion fully evaporate at temperatures above 375 °C. This means that some volatile manganese-containing species must be formed. To further investigate this observation, vacuum distillation of manganese from $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ was tried on a small scale, but in practice, the vapor pressures were too low for practical uses. Compounds with a triflate or methanesulfonate anion don't fully evaporate at temperatures below 450 °C. Comparing the first mass loss of all compounds with the same *N*-hexylimidazole ligand, $[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ is the most stable, followed by $[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$. $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$ already starts losing ligands at a lower temperature.

Fig. 2 TGA traces of the manganese(II) complexes with a sufficiently low melting temperature (< 120 °C) for electrochemical use. Heating rate: 5 °C min⁻¹ in N₂ atmosphere.

3.2 Crystal structures

Several manganese(II) complexes are solid at room temperature and upon recrystallization, a crystal structure could be determined. The crystal structure of the starting product $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ was determined first. From TGA and CHN measurements, it was already evident that the compound contains six molecules of water. The crystal structure (Figure 3) shows that all these six water molecules are coordinated to the manganese center and the bistriflimide anions are non-coordinating. All manganese atoms and bistriflimide anions in $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ are connected through C-H...O and C-H...N interactions, ranging from 2.762(3) Å to 3.130(4) Å. A summary of all interactions and bond lengths can be found in the ESI†.

Fig. 3 Crystal packing of $\text{Mn}(\text{Tf}_2\text{N})_2 \cdot 6\text{H}_2\text{O}$ viewed along the *c* axis. Dotted lines represent hydrogen bonds.

The crystal structure of $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$ is shown in Figure S1†. The manganese atom is coordinated in an octahedral configuration by six pyridine-*N*-oxide ligands that bond to the manganese atom through their oxygen atom. The compound crystallizes in the space group $P2_1/n$ and Mn-O distances vary from 2.122 Å to 2.181 Å. Several C-F... π interactions up to 3.837(3) Å were found, as well as several C-H...X interactions, ranging from 3.061(4) to 3.454(4) Å. A full analysis of all interactions and bond lengths can be found in the ESI†. A similar crystal structure was found for $[\text{Mn}(\text{MeIm})_6][\text{Tf}_2\text{N}]_2$ (Figure S2†), which has slightly larger Mn-N distances from 2.262 Å to 2.267 Å and crystallizes in the space group $P2_1/c$. Also C-H... π interactions are slightly larger (up to 3.5615(16) Å). $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$ crystallizes in the less symmetrical space group $P\bar{1}$ (Figure S3†) and has Mn-O distances of 2.163 Å to 2.193 Å which are slightly larger compared to Mn-O distances in $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$, indicating that pyridine-*N*-oxide is coordinated more strongly to the manganese center. In all three cases, the bistriflimide anions are non-coordinating.

Also several different glyme-ligands were used to coordinate to the manganese center. The crystal structure of $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$ is presented in Figure 4. The triglyme ligand is four-coordinating, and both bistriflimide anions coordinate to the manganese atom through an oxygen-manganese bond. This yields a distorted octahedral configuration. Interestingly, the Mn-O(bistriflimide) distance is shorter (2.162(1) Å) than the Mn-O(triglyme) distances (2.238(8) to 2.300(9) Å). The compound crystallizes in the space group $Fdd2$. There are only a few intra-molecular C-H...O interactions, ranging from 3.108(17) Å to 3.475(18) Å.

The crystal structure of the liquid manganese salt with a triflate anion, $[\text{Mn}(\text{G}_2)_1][\text{OTf}]_2$ is presented in Figure 5. The

Fig. 4 View of the crystal structure of $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$. Symmetry code: (i) $1-x, 1-y, z$.

asymmetric unit consists of one manganese center that is coordinated to all three oxygen atoms from the diglyme ligand, as well as to one oxygen from each triflate anion. Each asymmetric unit forms a dimer with another in which two anions act as bridging ligands between both metal centers. Again, Mn-O(triflate) distances are shorter (2.1079(15) Å to 2.1471(14) Å) than Mn-O(diglyme) distances (2.1739(14) Å to 2.2062(15) Å). A summary of the C-H...X interactions can be found in the ESI†.

Fig. 5 View of the crystal structure of $[\text{Mn}(\text{G}_2)_1][\text{OTf}]_2$. Symmetry code: (i) $2-x, 1-y, 1-z$.

When the recrystallized $[\text{Mn}(\text{G}_2)_1][\text{OTf}]_2$ was left open to the atmosphere for three days, the general appearance of the crystals had changed. Upon measuring the crystal structure of these crystals, a different space group was found ($Pm\bar{m}a$ instead of $P2_1/c$). In this new crystal structure, all triflate anions are bidentate and coordinate to two manganese atoms. The manganese atoms are also coordinated by two water ligands, making each center an almost undistorted octahedral (Figure 6). All diglyme moieties are non coordinating, but they are acting as the connection between each $\text{Mn}_2(\text{OTf})_4(\text{H}_2\text{O})_4$ -moiety through several C-H...O interactions ranging from 2.705(2) Å to 3.490(3) Å. All diglyme entities are connected to the water ligands through hydrogen bonds. Mn-O(triflate) distances are 2.1872(16) Å whereas Mn-O(water) interactions are shorter (2.104(2) Å and 2.119(2) Å).

Fig. 6 View of the crystal structure of $\text{Mn}_2(\text{OTf})_4(\text{H}_2\text{O})_4 \cdot (\text{G}_2)_2$. Symmetry codes: (i) $x, 1/2-y, z$; (ii) $1/2+x, 1/2-y, 1/2-z$; (iii) $1/2+x, y, 1/2-z$; (iv) $1+x, 1/2-y, z$; (v) $3/2+x, y, 1/2-z$; (vi) $1+x, y, z$; (vii) $3/2+x, 1/2-y, 1/2-z$. Dotted lines represent hydrogen bonds.

3.3 Electrochemistry

The electrochemical behavior of all liquid manganese salts with a sufficiently low melting point was investigated. First, the manganese deposition from $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ is described (Figure 7). A temperature of 50 °C was used since it was observed from TGA measurements that this compound thermally degrades after prolonged exposure to higher temperatures. In the cyclic voltammogram (CV), a small cathodic peak is observed at -0.5 V vs Fc^+/Fc (Fc = ferrocene) that is seemingly not related to any oxidation step of manganese (c_{ads} in Figure 7a). This is likely arising from adsorption of some species to the working electrode and a similar peak was observed in every liquid metal salt with a bistriflimide anion we have measured so far and it seems to be independent of the type of ligand that is used in the cation. A more detailed discussion on this matter can be found further on. At a more negative potential of -1.5 V vs Fc^+/Fc (Figure 7b), the bulk deposition of manganese metal starts. After removal of the electrode, a grey manganese layer was observed. On the reverse scan, there is only a small oxidation peak that can be ascribed to the oxidation of this deposited manganese layer. This irreversibility for the deposition of manganese from ionic liquids has been observed by Sun *et al.* as well.^{46,48–50} It is probably due to the sluggish chemical kinetics of the formation of the manganese(II) species. At very positive potentials (+2.0 V vs Fc^+/Fc), anodic decomposition occurs. This anodic process is unlikely to be the oxidation to Mn(III) since it is irreversible and is situated at a very high potential. In general, current densities in $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ are lower than those previously observed for copper(I) and silver(I) liquid metal salts, though this was to be expected since copper and silver are in an oxidation state of +I, whereas manganese is in the oxidation state of +II. The lower oxidation state for copper and silver causes a lower charge density of the cation, which results in less electrostatic interactions between anions and cations, resulting in a lower viscosity for copper(I) and silver(I) liquid metal salts, and hence better mass transport.^{10,23–26,28,30} The observed current densities for the manganese(II) salts are a factor of five smaller than what was found for the nickel(II) liquid metal salts.³³

$[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$ shows an electrochemical behavior identical to that of $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$. A small cathodic peak c_{ads} around +0.1 V vs Fc^+/Fc was observed which is probably

Fig. 7 Cyclic voltammograms of $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ on a Pt-coated silicon wafer working electrode. a) scan range -0.75 V to $+2.5 \text{ V}$ vs Fc^+/Fc showing the cathodic peak related to the anion c_{ads} ; b) scan range -2.25 V to $+1.75 \text{ V}$ vs Fc^+/Fc to show bulk deposition of manganese metal. The scans were recorded with $v_{\text{scan}} = 30 \text{ mV s}^{-1}$ and at $T = 50^\circ\text{C}$, a manganese plate was used as counter electrode and ferrocene/ferrocenium in $[\text{BMP}][\text{Tf}_2\text{N}]$ as reference electrode.

related to adsorption on the working electrode. At more negative potentials, an irreversible manganese deposition was observed. The triglyme ligand degradation occurs at more positive potentials than for $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ (Figure S4†).

Next, $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$ was investigated. In Figure 8a, the anodic scan of the cyclic voltammogram is presented. At $+0.75 \text{ V}$ vs Fc^+/Fc , an anodic peak is observed and upon reversing the scan direction, the corresponding cathodic peak of this process is found. Since the liquid manganese salt has a bright yellow color, it was possible to observe the working electrode during the experiment. Interestingly, a black layer was formed on top of the electrode. Since the deposit is formed at quite positive potential values, it could be the deposition of some manganese oxide species. Upon the reverse scan, this black layer is dissolved, indicating it cannot be degradation of the ligand or anion. Also the formation of a manganese oxide is unlikely, since this would probably not be electrochemically reversible since manganese oxide is not conductive, and due to the oxygen free environment of the glovebox, the formation of an oxide is highly unlikely. It was tried to remove the working electrode after keeping it at these positive potentials for some time, but this black layer easily delaminates. After several trials, a thin black layer could be investigated using grazing incidence X-ray

diffraction (XRD). When this X-ray spectrum is compared to that of $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$ (Figure S5†), the diffraction patterns are very similar, except for two small peaks at 2θ values of 29° and 46° . These two small peaks might arise from a slightly changed coordination environment between $\text{Mn}(\text{III})$ and $\text{Mn}(\text{II})$, but no additional peaks arise that indicate the formation of a manganese-oxide bond. Hence, we could conclude this reversible redox process in the cyclic voltammogram in Figure 8a and the resulting black layer on the working electrode must be from the oxidation of $\text{Mn}(\text{II})$ to $\text{Mn}(\text{III})$, and that this $\text{Mn}(\text{III})$ species is insoluble in the manganese LMS, causing what seems like a black deposited layer on the working electrode. On the cathodic scan in Figure 8b, first the small cathodic peak related to the adsorption c_{ads} is observed, after which a manganese deposit is formed at potentials below -2.0 V vs Fc^+/Fc , which is irreversible as well.

Fig. 8 Cyclic voltammograms of $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$ on a Pt-coated silicon wafer working electrode. a) scan range -1.25 V to $+1.75 \text{ V}$ vs Fc^+/Fc to show the cathodic peak related to the anion c_{ads} and the anodic $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple. Scan is started in anodic direction; b) scan range $+0.25 \text{ V}$ to -3.25 V vs Fc^+/Fc to show the bulk deposition of manganese metal. The scans were recorded with $v_{\text{scan}} = 30 \text{ mV s}^{-1}$ and at $T = 120^\circ\text{C}$, a manganese plate was used as counter electrode and ferrocene/ferrocenium in $[\text{BMP}][\text{Tf}_2\text{N}]$ as reference electrode.

For $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$, the small cathodic peak related to the adsorption c_{ads} was again observed around -0.25 V vs Fc^+/Fc , followed by the bulk deposition of manganese metal around -1.6 V vs Fc^+/Fc (Figure S6†). On the anodic side, a clear oxidation peak is observed, starting around $+1.0 \text{ V}$ vs Fc^+/Fc . It has a smaller shoulder around $+1.5 \text{ V}$ vs Fc^+/Fc . At potential values more positive than $+2.0 \text{ V}$ vs Fc^+/Fc , anodic degradation

occurs. The anodic process seems quasi-reversible, except for the shoulder. No black layer as in $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$ was observed, so this process must also be the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple, but in this case the $\text{Mn}(\text{III})$ species does not precipitate on the electrode.

The $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple was also found in $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$ (Figure 9). The anodic wave a_1 which is related to the oxidation to Mn^{3+} starts at a potential of +1.0 V vs Fc^+/Fc . Upon the reverse scan, a cathodic wave c_1 is measured with a peak around +0.3 V vs Fc^+/Fc . CVs recorded with a different anodic turning potential (Figure 9a) show that an increase in the anodic turning potential leads to an increase in the magnitude of the cathodic current c_1 . This indicates that c_1 and a_1 are linked and gives further evidence that these currents are related to the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple. At potential values above +1.7 V vs Fc^+/Fc , anodic decomposition of the electrolyte occurs.

Fig. 9 Cyclic voltammograms of $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$ on a Pt-coated silicon wafer working electrode. a) different positive vertex potentials were used; b) different scan rates indicate the quasi-reversibility of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple. The scans were recorded with $v_{\text{scan}} = 30 \text{ mV s}^{-1}$ and at $T = 120^\circ\text{C}$, a manganese plate was used as counter electrode and ferrocene/ferrocenium in $[\text{BMP}][\text{Tf}_2\text{N}]$ as reference electrode. Both scans were started in the anodic direction.

The reversibility of the redox couple was studied by recording CVs with different scanning rates and is depicted in Figure 9b.

It shows a typical quasi-reversible behavior for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple. Moreover, the inset in the same figure shows a linear correlation between the peak currents and the square root of the scan rate, indicating a diffusion controlled process. Nevertheless, when fitting the anodic currents, a non-zero intercept was obtained, which is likely due to the background current originating from the anodic decomposition of the liquid manganese salt.

On the cathodic scan in the CV of $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$ (Figure 10), two reduction waves are observed. c_{ads} is, as was observed for all earlier CVs, probably related to the adsorption on the working electrode, whereas c_2 corresponds to the reduction of $\text{Mn}(\text{II})$ to $\text{Mn}(0)$. On the backwards scan, only a small anodic wave is observed. At faster scan rates ($> 30 \text{ mV.s}^{-1}$), c_{ads} remains the same, whereas a_2 increases. This indicates these two waves are not related and a_2 must be the oxidation of Mn^0 . It is very clear from this CV that the $\text{Mn}^{2+}/\text{Mn}^0$ redox couple is not reversible. Very similar results are obtained for $[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ (Figure S7†).

Fig. 10 Cyclic voltammograms of $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$ on a Pt-coated silicon wafer working electrode. The scans were recorded with $v_{\text{scan}} = 30 \text{ mV s}^{-1}$ and at $T = 120^\circ\text{C}$, a manganese plate was used as counter electrode and ferrocene/ferrocenium in $[\text{BMP}][\text{Tf}_2\text{N}]$ as reference electrode.

In earlier experiments on nickel(II)-containing LMS $[\text{Ni}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ ³³, it was found using scanning tunneling microscopy measurements, that there is a potential-dependent adsorption of the ionic liquid onto the surface of the working electrode, blocking the electrode and hindering the electrodeposition of the nickel. Instead, nickel(0) nanoparticles were formed. The CVs from this liquid nickel salt are very similar to the one in Figure 10 and Figure S7†. Due to the similarity in the chemical structures of $[\text{Ni}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$, it was expected that no manganese deposits could be obtained from these liquid manganese salts but manganese(0) nanoparticles would be formed instead. Upon removal of the working electrode from the liquid manganese salt $[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ after the potential has been kept at -3.0 V vs Fc^+/Fc for 800 seconds, no manganese deposits were formed, but a black sludge was formed around the working electrode, which was completely

removed upon rinsing with acetone. When this rinsing acetone was investigated using transmission electron microscopy (TEM) by simply dropping the nanoparticle-containing acetone onto a TEM grid and evaporating the acetone, manganese nanoparticles were observed with a diameter smaller than 10 nm. Some of the particles cluster together to form structures of around 30 nm. These TEM images are very similar as well to what was observed in earlier experiments on $[\text{Ni}(\text{Helm})_6][\text{TF}_2\text{N}]_2$.

Fig. 11 Transmission electron microscopy image of manganese nanoparticles formed during electroplating from $[\text{Mn}(\text{Helm})_6][\text{TF}_2\text{N}]_2$ for 800 seconds at -3.0 V vs Fc^+/Fc . The nanoparticles are submerged in acetone.

The presence of the small cathodic peak c_{ads} seems to be independent on the type of ligand that is used to coordinate the manganese metal in the cation since it is present in every CV measured so far. Therefore, the anion was changed and the compound with a trifluoromethanesulfonate anion $[\text{Mn}(\text{Helm})_6][\text{OTf}]_2$ was synthesized and a cyclic voltammogram was measured. The working temperature was 100 °C since the melting temperature of this compound is 83 °C. No higher temperature could be used due to the rather limited thermal stability of this compound. It was found that Mn^{3+} could be formed and the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple is quasi-reversible (Figure 12a). Upon the reverse scan, two small cathodic peaks are found before the bulk deposition of manganese metal starts at -2.0 V vs Fc^+/Fc . Upon removal of the working electrode, a black manganese deposit was found. No formation of metallic nanoparticles was observed.

In Figure 12b, the two small cathodic peaks that arise before the bulk manganese metal deposition are further examined. c_2 and a_2 must be related, since the anodic peak a_3 does not occur when the scan rate is reversed immediately after c_2 (black line in Figure 12b). When a more negative vertex potential is used, c_3 arises, which is related to a_3 on the positive scan. In this case, a_2 is no longer present (blue dotted line). When a vertex potential in between c_2 and c_3 is used, the corresponding anodic peak is a convolution of a_2 and a_3 (red dashed line). This convolution of the peaks lead us to the conclusion that both small cathodic peaks must be related to the same process. From Figure 12c, it becomes apparent that the peaks c_2 and c_3 related to the adsorption have a lower current density than the same peaks that were observed for

Fig. 12 Cyclic voltammograms of $[\text{Mn}(\text{Helm})_6][\text{OTf}]_2$ on a Pt-coated silicon wafer working electrode. The scans were recorded with $v_{\text{scan}} = 30 \text{ mV s}^{-1}$ and at $T = 100 \text{ }^\circ\text{C}$, a manganese plate was used as counter electrode and ferrocene/ferrocenium in $[\text{BMP}][\text{TF}_2\text{N}]$ as reference electrode.

all compounds with a bistriflimide anion. For all compounds with a bistriflimide anion, c_{ads} was at least -0.1 A dm^{-2} and in several cases even higher, whereas for $[\text{Mn}(\text{Helm})_6][\text{OTf}]_2$, this peak is only 0.03 A dm^{-2} .

A cyclic voltammogram of the compound with the non fluorinated methanesulfonate anion $[\text{Mn}(\text{Helm})_6][\text{OMs}]_2$ was also measured (Figure 13). The melting temperature of $[\text{Mn}(\text{Helm})_6][\text{OMs}]_2$ is 103 °C, whereas thermal degradation already occurs around 120 °C. Therefore, a temperature of 115 °C was used, but since this is only slightly higher than the melting point of the compound, electrochemical kinetics are rather sluggish and hence, current densities in general are smaller than for other investigated compounds. As previously observed, the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple is quasi-reversible, as was the case for all manganese(II) salts in which the manganese

metal was coordinated by *N*-alkylimidazole ligands. At about -0.25 V vs Fc^+/Fc , the bulk deposition of manganese metal starts. This is at a significantly less negative potential than observed for any other manganese(II) liquid metal salt that were tested before. A grey metallic manganese deposit was obtained. Also, the peak corresponding to the adsorption is not present for this compound.

Fig. 13 Cyclic voltammograms of $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$ on a Pt-coated silicon wafer working electrode. The scans were recorded with $v_{\text{scan}} = 30 \text{ mV s}^{-1}$ and at $T = 115^\circ\text{C}$, a manganese plate was used as counter electrode and ferrocene/ferrocenium in $[\text{BMP}][\text{Tf}_2\text{N}]$ as reference electrode.

The cathodic peak c_{ads} is not observed at the same potential for every compound. It is situated between -0.4 and -1.3 V vs Fc^+/Fc , depending on the compound. This already gives an indication that this cathodic peak is not related to an electrochemical reaction, since it would then always be at a similar potential. It is more likely this peak is due to a surface effect of the working electrode. Also, when observing Figure 10, at scan rates above 30 mV s^{-1} , the peak current of the cathodic peak c_{ads} no longer increases with increasing scan rate. This can indicate that the electrochemical process is not reversible, or that full saturation of the surface of the working electrode is obtained and hence, currents no longer increase. Cyclic voltammograms showing a similar behavior were found in the literature. For example, Kolb *et al.*⁵⁸ measured a very similar cathodic peak in $[\text{BMIM}][\text{PF}_6]$. They characterized the nature of this cathodic peak and found it occurred at the potential where the adsorbed anions were exchanged for adsorbed cations. A similar cathodic process was also observed for $[\text{EMIM}][\text{Tf}_2\text{N}]$ and $[\text{BMIM}][\text{Tf}_2\text{N}]$,^{59,60} for $[\text{Py}_{14}][\text{FAP}]$ ($\text{FAP} = \text{tris}(\text{pentafluoroethyl})\text{trifluorophosphate}$)⁶¹ and $[\text{EMIM}][\text{FAP}]$ ⁶² and for $[\text{BMP}][\text{Tf}_2\text{N}]$ ⁶³. Recently, Magnussen *et al.* used *in situ* video-STM to study the adlayer structure of $[\text{HMIM}][\text{Cl}]$ and $[\text{HMIM}][\text{Tf}_2\text{N}]$ ($\text{HMIM} = 1\text{-hexyl-3-methylimidazolium}$).⁶⁴ Interestingly, they observed a similar cathodic peak in the CV of $[\text{HMIM}][\text{Tf}_2\text{N}]$ around the same potential than what was observed for manganese-containing liquid metal salts with a bistriflimide anion, whereas for $[\text{HMIM}][\text{Cl}]$, this peak was not present. They performed potential dependent *in situ* STM measurements and found that at these potentials, the orientation

of the adsorbed HMIM cation on the working electrode changed, causing a non-Faradaic current which was measured on the CVs. The orientation of the cation on the electrode was different for both ionic liquids, even though they had the same cation. Therefore, they concluded that the interaction between the anion and the adsorbing cation plays an important role on the orientation of this cation on the working electrode. It is very likely that a similar phenomenon occurs in our liquid metal salts. In an earlier paper, we reported STM images on $[\text{Ni}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ and found that a different species adsorbs on the electrode at negative potentials than at positive potentials.³³ We proposed in that work a possible mechanism for the electrochemical formation of nanoparticles from nickel-containing liquid metal salts based on this adsorption of the cathode on the working electrode. This adsorbed layer blocked the electrode, hindering the formation of nickel nuclei on the working electrode. Electrons have to tunnel through this adsorbed layer instead, forming Ni-adatoms at a certain distance from the electrode. These adatoms recombine to form nickel nanoparticles. For the nickel liquid metal salts however, we did not observe this c_{ads} . It is possible that this peak is present underneath the much larger peak from the bulk reduction of $\text{Ni}(\text{II})$ in the cyclic voltammograms since $\text{Ni}(\text{II})$ is reduced at a less negative potential than $\text{Mn}(\text{II})$. We already suspected a very similar mechanism for the nanoparticle formation from $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ than what was previously observed for nickel. The cyclic voltammograms of manganese look very similar to those of nickel (Figure 10) and nanoparticles were obtained (Figure 11), but no electrochemical nanoparticle formation was observed for manganese compounds with a triflate or methanesulfonate anion $[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$ and $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$. It is possible that the bistriflimide anion influences the adsorbed layer in the right way, causing the manganese adatoms to be formed at a suitable distance from the electrode to enable nanoparticle formation, whereas the triflate and methanesulfonate anions interact differently with the adsorbed cations and no nanoparticle are formed. Therefore, both the cation and anion play a role in the electrosynthesis of the nanoparticles.

The manganese deposits from $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{py-O})_6][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$ and $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$ were investigated using Scanning Electron Microscopy (SEM) (Figure 14). Deposits were made potentiostatically (-2.5 V vs Fc^+/Fc for $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$, -3.0 V vs Fc^+/Fc for $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$, -3.5 V vs Fc^+/Fc for $[\text{Mn}(\text{py-O})_6][\text{Tf}_2\text{N}]_2$, -3.0 V vs Fc^+/Fc for $[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$ and -3.5 V vs Fc^+/Fc for $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$) until at least -3.5 C cm^{-2} has passed in order to make the deposits sufficiently thick (theoretical thickness $2 \mu\text{m}$). Since some of the manganese layers delaminate very easily, the substrates were not rinsed with acetone but slowly submersed in a vial of acetone and left there for a few minutes before they are dried to remove residual ionic liquid. The deposits from $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ (Figure 14a) are cracked and seem to consist of hemispherical clusters with a diameter of several micrometer, which show subgrains of less

than 100 nm. The manganese deposits from $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$ (Figure 14b) consist of similar structures with subgrains, but the deposits in general are less cracked. The cathodic deposits from $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$ (Figure 14c) look very smooth with fine grains, although these deposits delaminate very easy, as was also the case for the anodic deposits that could be obtained from this ionic liquid. The final deposited layer was thinner than the theoretical thickness of 2 μm since it delaminates easily and a large part of the deposited manganese is lost upon washing the substrate with acetone. This becomes apparent from the small manganese peaks and the presence of large silicon and platinum peaks on the elemental analysis (EDX, Figure S8†), since the latter two arise from the underlying platinum coated silicon substrate that is still visible through the thin manganese layer. The manganese deposit from $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$ (Figure 14d) is very similar to what was previously observed for nickel deposits from $[\text{Ni}(\text{EtIm})_3(\text{HeIm})_3][\text{Tf}_2\text{N}]_2$ and is also most similar to what Sun *et al.*^{46–50} observed for their manganese deposits. The deposited layers consist of many small spheres, each with a diameter smaller than 100 nm. The deposits from $[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$ (Figure 14e) consist of a smooth layer with fine grains. The same observations were made for $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$ (Figure 14f), but interestingly, a few large spheres ($> 1 \mu\text{m}$) are observed that consist of pure manganese according to EDX. The background behind these spheres consists of very smooth manganese. On the elemental analysis (EDX) spectra of all compounds, manganese peaks were observed as the only metallic species. Oxygen peaks were observed as well, since elemental manganese is easily oxidized under atmospheric conditions, hence the oxygen peaks arise from oxidation of the deposited layer after removal of the deposit from the glove box and before they were observed in the SEM. A sulfur peak was also observed for several compounds. This must be from the anion, since the SO_2 and SO_3 groups of the anions are the only available sources of sulfur. Manganese has a strong affinity for sulfur. For this reason, manganese is used in steel production to bind sulfur and manganese can even be used for desulfurization of gases.^{66,67}

3.4 Conclusions

Manganese metal was electrodeposited from liquid manganese(II) salts with glyme ligands, pyridine-*N*-oxide, DMSO and imidazole-type ligands. Chemical characterization of all liquids was performed, crystal structures were determined and discussed, and their electrochemical properties were tested. It was found that the liquid manganese salts with glyme-type ligands were very hygroscopic and after prolonged exposure to the atmosphere, ligand exchange was observed when the diglyme ligand in $[\text{Mn}(\text{G}_2)_1][\text{OTf}]_2$ became non-coordinating and the species $\text{Mn}_2(\text{H}_2\text{O})_4(\text{OTf})_4 \cdot (\text{G}_2)_2$ was formed. From $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$, slightly cracked manganese metal depositions were obtained and it was found that Mn(III) was not stable in these liquids. In $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$, a reversible anodic deposition was observed, which was found to

Fig. 14 Top-view SEM micrographs of potentiostatically electroplated manganese thin films deposited from a) $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$, b) $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$, c) $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$, d) $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$, e) $[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$ and f) $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$.

be an insoluble Mn(III) species that precipitated on the electrode. From $[\text{Mn}(\text{py}-\text{O})_6][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{G}_2)_2][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{G}_3)_1][\text{Tf}_2\text{N}]_2$, manganese deposits were obtained. In $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$, no deposition of a manganese metal layer was observed but manganese nanoparticles were formed with 100% efficiency, as was also the case for earlier published results on the liquid nickel(II) salt $[\text{Ni}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$. The $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple was found to be quasi-reversible in $[\text{Mn}(\text{BuIm})_6][\text{Tf}_2\text{N}]_2$, $[\text{Mn}(\text{HeIm})_6][\text{Tf}_2\text{N}]_2$ and $[\text{Mn}(\text{DMSO})_6][\text{Tf}_2\text{N}]_2$. A small cathodic peak was observed for all cyclic voltammograms of manganese(II) containing ionic liquids with a bistriflimide anion, which was also present to a lesser extent in $[\text{Mn}(\text{HeIm})_6][\text{OTf}]_2$ but was not present in $[\text{Mn}(\text{HeIm})_6][\text{OMs}]_2$. From literature reports, it became clear that this was due to a non-Faradaic current originating from changes in the conformation of the adsorbed cation on the working electrode. The influence of the anion on this adsorbed cation has been described before and also became apparent in this case. Hence, not only the nature of the cation determines whether a manganese layer can be deposited or manganese nanoparticles are formed electrochemically, the role of the anion can neither be ignored.

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Table of contents graphic

Manganese(II)-containing ionic liquids with different ligands and anions were prepared. Electrodeposition of manganese or electrosynthesis of manganese nanoparticles was observed, depending on the chemical structure of the ionic liquid.