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High current density electrodeposition of silver from silver-containing liquid metal salts with pyridine-*N*-oxide ligands

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Ionic silver(I) complexes of pyridine-*N*-oxide with bis(trifluoromethanesulfonyl)imide, trifluoromethanesulfonate, methanesulfonate and nitrate anions were structurally characterized and used in the molten state as electrolytes for the electrodeposition of silver coatings.

Keywords: electrodeposition; ionic liquids; liquid metal salts; silver; X-ray crystallography

Abstract

New cationic silver-containing ionic liquids were synthesized and used as non-aqueous electrolytes for the electrodeposition of silver layers. In the liquid state of these ionic liquids, a silver cation is coordinated by pyridine-*N*-oxide (py-O) ligands in a 1:3 metal-to-ligand ratio, although in some cases a different stoichiometry of the silver center crystallized out. As anions, bis(trifluoromethanesulfonyl)imide (Tf₂N), trifluoromethanesulfonate (OTf), methanesulfonate (OMs) and nitrate were used, yielding compounds with the formulae [Ag(py-O)₃][Tf₂N], [Ag(py-O)₃][OTf], [Ag(py-O)₃][OMs] and [Ag(py-O)₃][NO₃], respectively. The compounds were characterized by CHN analysis, FTIR, NMR, DSC, TGA and the electrodeposition of silver was investigated by cyclic voltammetry, linear potential scan, scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX). With the exception of [Ag(py-O)₃][Tf₂N], which melts at 108 °C, all the silver(I) compounds had a melting point below 80 °C and were tested as electrolytes for silver electrodeposition. Interestingly, very high current densities were observed at a potential of -0.5 V vs Ag/Ag⁺ for the compounds with fluorine-free anions, i.e. [Ag(py-O)₃][NO₃] (current density of -10 A dm⁻²) and [Ag(py-O)₃][OMs] (-6.5 A dm⁻²). The maximum current density of the compound with the fluorinated anion trifluoromethanesulfonate, [Ag(py-O)₃][OTf], was much lower: -2.5 A dm⁻² at -0.5 V vs Ag/Ag⁺. Addition of an excess of ligand to [Ag(py-O)₃][OTf] resulted in the formation of the room-temperature ionic liquid [Ag(py-O)₆][OTf]. A current density of -5 A dm⁻² was observed at -0.5 V vs Ag/Ag⁺ for this low viscous silver salt. The crystal structures of several silver complexes could be determined by X-ray diffraction, and it was found that several of them had a stoichiometry different from the 1:3 metal-to-ligand ratio used in their synthesis. This indicates that the compounds form crystals with a composition different from that of the molten state. The

electrochemical properties were measured in the liquid state, where the metal-to-ligand ratio was 1:3. Single crystal X-ray diffraction measurements showed that silver(I) is six coordinate in $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$ and $[\text{Ag}(\text{py-O})_3][\text{OTf}]$, while it is five coordinate in the other complexes. In $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$, there are two different coordination environments for silver ions: six coordinate central silver ions and five coordinate for the outer silver ions. In some of the silver(I) complexes, silver-silver interactions were observed in the solid state.

Introduction

Ionic liquids are solvents that consist entirely of ions.¹ They are very useful for electrochemical applications because of their wide electrochemical window and the presence of intrinsic ionic charge carriers.² Disadvantages are their usually high viscosity and low solubility for metal ions.³ By incorporating a metal ion into the molecular structure of the ionic liquid, high metal concentrations can be achieved. If this metal is incorporated into the cation, it will electromigrate to the cathode during electrodeposition, allowing a better mass transport to counteract the higher viscosity of the ionic liquid. The cathodic reaction of these ionic liquids is the deposition of metal, so that there are no issues with the cathodic decomposition of the ionic liquid components. Only a few examples of these “liquid metal salts” can be found in the literature,^{4,5,6,7} and their use for electrochemical purposes has only been rather scarcely investigated.^{8,9,10,11,12,13,14} Our research group recently pointed to the potential of these liquid metal salts as electrolytes for the high-rate electrodeposition of copper,^{15,16,17} and silver.^{18,19,20} Current densities up to -25 A dm^{-2} at a potential of -10 V vs Ag/Ag^+ (without compensation for the IR drop) were achieved for $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ ¹⁵ and current densities up to -20 A dm^{-2} at -10 V (without IR drop compensation) for $[\text{Ag}(\text{MeCN})_4]_2[\text{Ag}(\text{Tf}_2\text{N})_3]$.¹⁸ Metal deposits of a good quality could be obtained, even without the use of additives, although the smoothness of the deposited layer significantly increased upon addition of thiourea or 1-*H*-benzotriazole to the electrolyte in the case of $[\text{Ag}(\text{MeCN})_4]_2[\text{Ag}(\text{Tf}_2\text{N})_3]$.¹⁸

In this paper, we describe new silver-containing liquid metal salts with pyridine-*N*-oxide ligands (py-O) and several different anions: bis(trifluoromethanesulfonyl)imide (bistriflimide, Tf_2N), trifluoromethanesulfonate (triflate, OTf) and the non-fluorinated anions methanesulfonate (mesylate, OMs) and nitrate (NO_3). The metal-to-ligand ratios were in general 1:3, although in

some cases compounds with different stoichiometries crystallized, as evidenced by single crystal X-ray diffraction studies. The electrochemistry of the silver-containing liquid metal salts was studied and the compounds were used for the electrodeposition of silver coatings. Also a compound of stoichiometry 1:6, $[\text{Ag}(\text{py-O})_6][\text{OTf}]$, was studied by electrochemistry

Experimental

General

All chemicals were purchased from IoLiTec (Heilbronn, Germany) or Sigma-Aldrich (Bornem, Belgium) and were of reagent grade and were used as received. The infrared spectra were recorded at a resolution of 4 cm^{-1} , using an attenuated total reflectance (ATR) technique on a Bruker Vertex 70 FTIR spectrometer, with a Platinum ATR extension. Assignment of the peaks was based on available literature.²¹ Melting points were determined on a Mettler-Toledo 822 DSC instrument at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a helium atmosphere. TGA studies were performed on a TA instruments Q600 thermogravimeter from room temperature up to $400\text{ }^{\circ}\text{C}$ at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. The morphology and elemental composition of the silver deposits were determined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX) (Philips XL 30 FEG). The viscosities were measured on a Brookfield cone plate viscometer (LVDV-II+ programmable viscometer) with a cone spindle CPE-40. The sample holder was heated to $80\text{ }^{\circ}\text{C}$ by a circulating water bath. Elemental analyses (C, H, N) were carried out using a CE Instruments EA-1110 elemental analyzer. For most compounds however, a different metal-to-ligand stoichiometry crystallized out than the 1:3 ratio that was

synthesized. This made homogeneous sample preparation for CHN analysis challenging. When the samples were heated until above their melting temperature, silver CHN cups could be filled with the appropriate amount of compound while maintaining a 1:3 metal-to-ligand ratio. Since sample preparation for CHN requires very precise mass measurements, this requires some time during which the water soluble compounds $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ and $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ absorbed atmospheric moisture. The other compounds were not water soluble and also no traces of water were found in their CHN results. From the compound $[\text{Ag}(\text{py-O})_3][\text{OTf}]$, the compound $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$ crystallized out, which was also found in the CHN analysis of those crystals. For $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$, CHN sample preparation was more straightforward since this compound crystallizes in the same metal-to-ligand ratio. Since the water soluble compounds were immediately brought in the inert atmosphere of the glove box after synthesis and drying, the water that was absorbed during sample preparation for the CHN measurements was not present during the electrochemical experiments.

Electrochemistry

Gold-covered silicon wafers were used as the working electrode for electrodeposition. In order to make the current density uniform across the whole electrode area, the electrode was recessed by placing it inside a PTFE sample holder, which decreased the tendency for dendritic growth and defines the area of the working electrode. The presence of dendrites increases the real surface area which means that the real current density is lower than the value based on the geometrical surface area of the electrode. A complete description of the electrochemical cell is given elsewhere.¹⁵ Before use, the substrates were cleaned by rinsing with acetone and dried. After the

deposition of a silver layer, the deposit was rinsed with water and acetone and dried. The electrolyte was contained in a platinum crucible, and it was not stirred during the experiments. The electrochemical experiments were conducted at 90 °C. The experiments were performed using a Solartron Instruments SI 1287 electrochemical interface controlled by a computer with Corrware software. All potential values in this paper are relative to a silver wire directly immersed in solution (pseudo-reference electrode). The potential values were corrected for the iR drop in real time by using the current interrupt technique as was also described elsewhere.¹⁵ A silver coil was used as counter electrode. It is known that ionic liquids, even the most hydrophobic ones, can take up atmospheric moisture which might alter the deposit morphology, depending on the amount of absorbed water.²² Therefore, all electrochemical experiments were performed in an argon-filled glove box (with oxygen and water concentrations below 1 ppm).

Crystallography

Crystals that were grown from the compounds with the general formula $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$, $[\text{Ag}(\text{py-O})_3][\text{OTf}]$, $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ and $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ which were suitable for single crystal X-ray diffraction were mounted on a nylon loop attached to a copper pin and placed on an Agilent SuperNova diffractometer into the cold stream of an Oxford Cryostream 700 at 100(2) K using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The absorption corrections were applied using CrysAlisPro.²³ All structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELXL.²⁴ For refinement and making pictures, the program OLEX2 was used.²⁵ All hydrogen atoms were placed in calculated positions and refined using a riding model. For the crystal structure of the α -polymorph of $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$, the bistriflimide

anions were disordered over two positions. For one of the anions, the major disorder part comprised 72.4(5)% of the total and for the other it was 78.9(1)%. For the β -polymorph, also one of the bis(trifluoromethanesulfonyl)imide anions was disordered over two positions. The major disorder part here comprised 65.6(7)% of the total occupancy. Appropriate restraints on bond distances and thermal parameters were used. CCDC 958484-958489 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

AgOTf: To silver(I) oxide (1.00 g, 4.38 mmol) in tetrahydrofuran (25 mL) was added trifluoromethanesulfonic acid (1.32 g, 8.77 mmol) and stirred for 1 hour at room temperature. Solvent was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a white solid. Yield: 2.145 g (95%). CHN found (calculated for AgCF_3SO_3): C 4.42 (4.67) %, H 0.00 (0.00) %, N 0.00 (0.00) %. IR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 1233 (CF_3), 1194 (CF_3), 1005, 616, 578 (CF_3), 574 (CF_3). Melting point: > 200 °C.

AgOMs: To silver(I) oxide (1.00 g, 4.38 mmol) in acetonitrile (25 mL) was added methanesulfonic acid (0.84 g, 8.77 mmol) and stirred for 1 hour at room temperature. Solvent was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a white solid. Yield: 1.696 g (95%). CHN found (calculated for AgCH_3SO_3): C 6.13 (5.92) %, H 1.98 (2.21) %, N: 0.00 (0.00) %. IR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 1700, 1338, 1116, 1016, 770, 514. Melting point: >200 °C.

[Ag(py-O)₃][OTf]: To silver(I) triflate (10.0 g, 38.9 mmol) in acetonitrile (25 mL) was added pyridine-*N*-oxide (11.1 g, 116.8 mmol) and stirred for 1 hour at room temperature. Excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a brown solid. Yield: 20.88 g (99%). CHN found (calculated for C₄₃H₄₀Ag₃F₉N₈O₁₄S₃): C 34.73 (34.81) %, H 3.10 (2.72) %, N 7.32 (7.55) %. IR (ATR, $\nu_{\max}/\text{cm}^{-1}$): 3115 (CH), 3077 (CH), 3021 (CH), 2941 (CH), 2863 (CH), 1607 (ring), 1464 (ring), 1262, 1213 (NO)/(CF₃), 1168 (CH in plane), 1152 (CH in plane), 1070 (CH in plane), 1026 (ring breathing), 1018 (ring breathing), 915, 830 (NO.), 763 (CH out of plane), 699, 631, 572 (CF₃), 549, 514, 487, 476; NMR: δ_{H} (400 MHz, DMSO-*d*₆): 8.39 (m), 7.37 (m), 2.20 (s); δ_{C} (100 MHz, DMSO-*d*₆): 140.12 (s), 127.83 (s), 126.49 (s), 120.39 (q), 35.97 (m); Melting point: 76 °C; Viscosity: 35 mPa.s (80 °C).

[Ag(py-O)₂][OMs]: To silver(I) methanesulfonate (1.00 g, 4.93 mmol) in acetonitrile (25 mL) was added pyridine-*N*-oxide (0.94 g, 9.90 mmol) and stirred for 1 hour at room temperature. Excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a light brown solid at room temperature. Yield: 1.93 g (99%). CHN found (calculated for C₁₁H₁₃AgN₂O₅S): C 33.37 (33.60) %, H 3.21 (3.33) %, N 6.87 (7.12) %. IR (ATR, $\nu_{\max}/\text{cm}^{-1}$): 3101 (CH), 3073 (CH), 3016 (CH), 2939 (CH), 1463 (ring), 1208 (NO), 1189, 1164 (CH in plane), 1072 (CH in plane), 1035, 1016 (ring breathing), 821 (NO), 781, 760 (CH out of plane), 673, 547, 524, 491, 473; NMR: δ_{H} (400 MHz, DMSO-*d*₆): 8.24 (m), 7.31 (m), 1.99 (s); δ_{C} (100 MHz, DMSO-*d*₆): 138.85 (s), 126.71 (s), 125.61 (s), 77.32 (s), 77.01 (s), 76.67 (s) ; Melting point: 86 °C.

[Ag(py-O)₃][OMs]: To silver(I) methanesulfonate (10.0 g, 49.3 mmol) in acetonitrile (25 mL) was added pyridine-*N*-oxide (14.06 g, 147.8 mmol) and stirred for 1 hour at room temperature.

Excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a light brown liquid at room temperature. Yield: 23.59 g (98%). After a few days, the product slowly solidifies to a glassy solid. CHN found (calculated for $C_{16}H_{18}AgN_3O_6S \cdot H_2O$): C 38.08 (37.96) %, H 4.35 (3.98) %, N 8.29 (8.30) %. IR (ATR, $\nu_{\max}/\text{cm}^{-1}$): 3101 (CH), 3071 (CH), 3015 (CH), 2938 (CH), 1606 (ring), 1461 (ring), 1419 (SO_2), 1325 (SO_2), 1209 (NO), 1166 (CH in plane), 1071 (CH in plane), 1035, 1015 (ring breathing), 931, 915, 832 (NO), 761 (CH out of plane), 673, 546, 523, 491, 468; NMR: δ_H (300 MHz, CDCl_3): 8.22 (m), 7.28 (m), 1.95 (s); δ_C (75 MHz, CDCl_3): 139.43 (s), 126.16 (s), 125.91 (s), 77.47 (s), 77.04 (s), 76.62 (s); Melting point: 77 °C; Viscosity: 22 mPa.s (80 °C).

[Ag(py-O)₂][NO₃]: To silver(I) nitrate (1.00 g, 5.89 mmol) in acetonitrile (25 mL) was added pyridine-*N*-oxide (1.12 g, 11.78 mmol) and stirred for 1 hour at room temperature. Excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a light brown solid at room temperature. Yield: 2.06 g (97%). CHN found (calculated for $C_{10}H_{10}AgN_3O_5S$): C 33.10 (33.35) %, H 2.28 (2.79) %, N 11.42 (11.67) %. IR (ATR, $\nu_{\max}/\text{cm}^{-1}$): 3103 (CH), 3074 (CH), 3054 (CH), 1463 (ring), 1409 (NO from anion), 1290 (NO from anion), 1207 (NO from py-O), 1174 (CH in plane), 1147 (CH in plane), 1072 (CH in plane), 1033 (ring breathing), 1018 (ring breathing), 925, 831 (NO from py-O), 819, 760 (CH out of plane), 671, 551, 510, 492, 475; NMR: δ_H (400 MHz, DMSO-d_6): 8.21 (m), 7.37 (m), 1.91 (s); δ_C (100 MHz, DMSO-d_6): 138.81 (s), 126.69 (s), 124.91 (s); Melting point: 44 °C.

[Ag(py-O)₃][NO₃]: To silver(I) nitrate (3.00 g, 17.7 mmol) in acetonitrile (25 mL) was added pyridine-*N*-oxide (5.04 g, 53.1 mmol) and stirred for 1 hour at room temperature. Excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a light brown liquid at room temperature. Yield: 7.976 g (99%). After a

few days, the product slowly crystallizes. CHN found (calculated for $C_{15}H_{15}AgN_4O_6 \cdot H_2O$): C 37.89 (38.07) %, H 3.92 (3.62) %, N 11.72 (11.84) %. IR (ATR, $\nu_{\max}/\text{cm}^{-1}$): 3380 (H_2O), 3104 (CH), 3074 (CH), 3054 (CH), 3018 (CH), 1607 (ring), 1463 (ring), 1405 (NO from anion), 1291 (NO from anion), 1208 (NO from py-O), 1173 (CH in plane), 1147 (CH in plane), 1072 (CH in plane), 1033 (ring breathing), 1017 (ring breathing), 925, 831 (NO from py-O), 820, 761 (CH out of plane), 671, 550, 509, 491, 475; NMR: δ_H (300 MHz, $CDCl_3$): 8.22 (m), 7.28 (m), 1.93 (s); δ_C (75 MHz, $CDCl_3$): 139.44 (s), 126.17 (s), 125.95 (s), 77.49 (s), 77.06 (s), 76.64 (s); Melting point: 67 °C; Viscosity: 17.5 mPa.s (80 °C).

[Ag(py-O)₆][OTf]: To silver(I) triflate (10.0 g, 38.9 mmol) in acetonitrile (25 mL) was added pyridine-*N*-oxide (22.2 g, 233.4 mmol) and stirred for 1 hour at room temperature. Excess of acetonitrile was removed on a rotary evaporator and the product was dried overnight on a high vacuum line, yielding a brown liquid at room temperature. Yield: 30.26 g (94%). After a few days, small crystals submersed in this liquid arise. Single crystal X-ray diffraction characterized the crystals to be [Ag(py-O)₃][OTf]. CHN found (calculated for $C_{31}H_{30}AgF_3N_6O_9S$): C 44.87 (44.99) %, H 4.01 (3.65) %, N 9.98 (10.15) %. IR (ATR, $\nu_{\max}/\text{cm}^{-1}$): 3115 (CH), 3077 (CH), 3052 (CH), 3021 (CH), 1606 (ring), 1463 (ring), 1262, 1214 (NO)/(CF₃), 1169 (CH in plane), 1153 (CH in plane), 1026 (ring breathing), 1017 (ring breathing), 830 (NO), 763 (CH out of plane), 670, 631, 572 (CF₃), 548, 514, 477; NMR: δ_H (400 MHz, DMSO-*d*₆): 8.36 (m), 7.34 (m), 2.19 (s); δ_C (100 MHz, DMSO-*d*₆): 139.71 (s), 127.51 (s), 126.19 (s), 120.24 (q), 36.01 (m); Melting point: < RT.; Viscosity: 8 mPa.s (80 °C).

[Ag(py-O)₃][Tf₂N]: To [Ag(MeCN)][Tf₂N], which was synthesized as described earlier¹⁶ (5 g, 11.6 mmol) in acetonitrile (25 mL) was added pyridine-*N*-oxide (3.31 g, 34.8 mmol) and stirred for 1 hour at room temperature. Excess of acetonitrile was removed on a rotary evaporator and

the product was dried overnight on a high vacuum line, yielding a light brown solid at room temperature. Yield: 15.56 g (99%). CHN found (calculated for $C_{17}AgF_6N_4O_7S_2H_{15}$): C 30.23 (30.33) %, H 2.39 (2.25) %, N 8.13 (8.32) %. IR (ATR, $\nu_{\max}/\text{cm}^{-1}$): 3111 (CH), 3059 (CH), 3025 (CH), 1466 (ring), 1350, 1332, 1172 (CH in plane), 1135 (SO_2), 1050 (SNS), 1017 (ring breathing), 830 (NO), 762 (CH out of plane), 739 (CF_3), 672, 602 (SO_2), 569, 550, 508, 476. NMR: δ_{H} (400 MHz, DMSO-d_6): 8.29 (m), 7.22 (m), 2.08 (s); δ_{C} (100 MHz, DMSO-d_6): 139.32 (s), 127.10 (s), 126.01 (s), 119.96 (q), 39.98 (m); Melting point: 108 °C.

Results and Discussion

Synthesis

Starting reagents AgOTf, AgOMs and $[\text{Ag}(\text{MeCN})][\text{Tf}_2\text{N}]$ were prepared for the synthesis of the liquid metal salts described in this manuscript. To these starting reagents, pyridine-*N*-oxide (py-O) was added in a 1:3 metal-to-ligand ratio. In one case a 1:6 ratio was used for $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ to test the influence of an excess of ligand. Acetonitrile was used as solvent and was removed *in vacuo* after the reaction. The product was dried overnight on a Schlenk line at room temperature until the acetonitrile solvent no longer appeared on the FTIR or NMR spectra. For $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$, commercially available silver(I) nitrate was used as a starting reagent and the py-O ligand was added in a 1:3 stoichiometry. All products were originally obtained as supercooled liquids, but they crystallized spontaneously after a few days in the storage vessel. Only the first crystallization required a longer time. In some cases, the crystals were suitable to be studied by single crystal diffraction and are described below. In most cases the compound that crystallized from the melt had a different ligand-to-metal stoichiometry in the crystalline state

than in the liquid state. The melting temperatures of most of the compounds were between 65 °C and 80 °C. Therefore, electrochemical measurements were performed at 90 °C. Only [Ag(py-O)₆][OTf] was a liquid at room temperature, but this also formed some small crystals submersed in the liquid after a few days. [Ag(py-O)₃][Tf₂N] had a melting temperature of 108 °C (Table 1). Interestingly, the compound with the bis(trifluoromethanesulfonyl)imide anion, [Ag(py-O)₃][Tf₂N] was the only compound which melts above 100 °C. This was unexpected, because the bis(trifluoromethanesulfonyl)imide anion yields in general ionic liquids with low melting points and low viscosities. The electrochemical properties of [Ag(py-O)₃][Tf₂N] were therefore not investigated, due to the compound's high melting point.

[Insert Table 1]

Crystal structures

The crystal structures of all crystalline silver(I) complexes with pyridine-*N*-oxide ligands were determined by single-crystal X-ray diffraction. The crystallographic data are summarized in Table 2. The crystallographic asymmetric unit of [Ag(py-O)₃][Tf₂N] contains six silver atoms, six pyridine-*N*-oxide ligands and two bis(trifluoromethanesulfonyl)imide anions in the highly symmetric space group *P31c*. All six of the silver atoms lie on a threefold rotation axis with the py-O molecules and Tf₂N anions occupying general positions. Each py-O ligand is bidentate and coordinates to two adjacent silver atoms and each silver atom is coordinated by six py-O ligands creating linear one-dimensional chains (Figure 1). Adjacent Ag atoms along the chain are close enough to each other so that they are involved in Ag...Ag interactions with Ag...Ag distances

varying from 3.0244(7) Å to 3.247(1) Å (Table S1). As a consequence of the space group symmetry and the location of the silver centers in the unit cell, there are actually two crystallographically unique one-dimensional chains, as can be seen in the packing diagram (Figure S1). Both chains run parallel to the crystallographic *c* axis, but those which are at the unit cell corners are different to those at positions (1/3, 2/3, *c*) and (2/3, 1/3, *c*). The former chains have two crystallographically distinct silver centers and it is possible to observe nine Ag-O bonds looking down the chain, whilst the latter chains contain four silver centers and there are 12 Ag-O bonds visible. The bis(trifluoromethanesulfonyl)imide anions occupy the positions between the chains (Figure S1). There are also π - π interactions between the py-O ligands, as summarized in Table S2.

A different polymorph was also crystallized upon addition of an excess of py-O ligand to [Ag(py-O)₃][Tf₂N]. The molecular structure is essentially the same as the polymorph that was just described, with silver centers linked by three bridging py-O ligands to create one dimensional chains of six coordinate silver centers augmented by Ag...Ag interactions (Figure S2). This polymorph also possesses high symmetry and is in the rhombohedral space group *R*-3, but in this instance there are 10 independent silver centers (all on symmetry elements), nine independent py-O ligands and three independent bis(trifluoromethanesulfonyl)imide anions. Looking perpendicularly to the chains, it is possible to see the many different orientations of py-O ligands around the central axis (Figure 2). The Ag-O distances range from 2.4492(2) Å to 2.513(2) Å. The Ag...Ag distances range from 3.0417(4) Å to 3.2239(4) Å (Table S1). The π - π interactions are presented in Table S2. [Ag(py-O)₃][Tf₂N] has a high melting temperature of 108 °C, which makes it less interesting for electrochemical characterization. Due to the high melting

point of $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$, different anions were tested to see if they resulted in compounds with lower melting points.

[Insert Table 2]

[Insert Figures 1-2]

The solid state structure of $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$ was crystallized from $[\text{Ag}(\text{py-O})_3][\text{OTf}]$, showing that the compound that crystallizes does not always have the same composition as the bulk solution. The asymmetric unit of $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$ was found to have three silver atoms, eight py-O ligands and three trifluoromethanesulfonate anions in the crystallographic asymmetric unit (Figure S3). The $[\text{Ag}_3(\text{py-O})_8]$ cationic unit is a pseudo-centrosymmetric linear moiety with the central silver atom being six coordinate and the outer two silver atoms are five coordinate. The range of Ag–O bond distances for the six coordinate silver atom are 2.413(3) Å to 2.559(3) Å and for the two five coordinate silver atoms are 2.270(3) to 2.598(3) Å and 2.249(3) Å to 2.632(3) Å (Table S1). Although the Ag–O distance of 2.632(3) Å is longer than the sum of the bonding radii for Ag and O, it is still considered as a bond because it is only ca. 0.05 Å longer than the next longest bond. There are also long Ag...Ag interactions (Ag–Ag = 3.2916(5) Å and 3.3210(5) Å) within the $[\text{Ag}_3(\text{py-O})_8]$ moiety. Of the eight py-O molecules, two (those containing O1 and O50) coordinate in a monodentate fashion, four (O8, O22, O36 and O43) are bidentate bridging two separate silver atoms and two (O15 and O29) are tridentate bridging three separate atoms. The central six coordinate silver atom of the $[\text{Ag}_3(\text{py-O})_8]$ moiety is connected to each of its two silver neighbors through three py-O ligands, in a similar way to that seen in the

structures of $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ and $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$. The outer five coordinate silver atoms are connected to silver atoms of symmetry related $[\text{Ag}_3(\text{py-O})_8]$ moieties through only two py-O ligands (Figure 3), but these are the two py-O ligands that are tridentate, also coordinating one of the central silver atoms of the $[\text{Ag}_3(\text{py-O})_8]$ moiety. Through these two py-O ligands, the $[\text{Ag}_3(\text{py-O})_8]$ moieties form a one-dimensional chain structure parallel to the crystallographic a axis (Figure 3). The $\text{Ag}\cdots\text{Ag}$ distance between two different $[\text{Ag}_3(\text{py-O})_8]$ moieties is 3.4800(5) Å, which is longer than $\text{Ag}\cdots\text{Ag}$ distances within the $[\text{Ag}_3(\text{py-O})_8]$ unit and probably too long to be a $\text{Ag}\cdots\text{Ag}$ interaction. The trifluoromethanesulfonate anions are totally non-coordinating and occupy positions in the crystal lattice between the $[\text{Ag}_3(\text{py-O})_8]_\infty$ chains (Figure S4). The packing diagram viewed along the crystallographic a axis (Figure S4) shows that there are π - π interactions between the pyridine rings along the $[\text{Ag}_3(\text{py-O})_8]_\infty$ chains. The π - π interactions are relatively strong with plane-centroid distances as low as 3.187 Å (see Table S2 for details).

[Insert Figure 3]

Single crystals of $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ were grown from a liquid with the composition $[\text{Ag}(\text{py-O})_6][\text{OTf}]$. The crystallographic asymmetric unit of $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ was found to contain one silver atom coordinated by three py-O ligands and one non-coordinating trifluoromethanesulfonate anion. Ag-O distances vary between 2.3652(1) Å and 2.5117(1) Å (Table S1). This longest distance is significantly larger than the sum of the atomic radii of silver and oxygen so this interaction cannot be considered as a true bond, but it is considerably shorter than the sum of the van der Waals radii. Thus each silver center can be considered as having a

[5+1] coordination environment. Each silver center is connected to another through three bridging py-O ligands giving rise to $[\text{Ag}(\text{py-O})_3]_\infty$ moieties that form a one-dimensional chain structure parallel to the crystallographic *c* axis (Figures S5 and S6). There is also a $\text{Ag}\cdots\text{Ag}$ interaction along the chain with a distance of 3.0190(2) Å. The π - π interactions are presented in Table S2. The trifluoromethanesulfonate anions occupy positions in between the $[\text{Ag}(\text{py-O})_3]_\infty$ chains. This is rather similar to what is found when looking at the *c* axis in the packing of the crystal structure of both polymorphic forms of $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$, only the angle between three consecutive silver centers is not linear but 163.197(5)°.

From the compound $[\text{Ag}(\text{py-O})_3][\text{OMs}]$, single crystals of $[\text{Ag}(\text{py-O})_2][\text{OMs}]$ were obtained. The asymmetric unit of $[\text{Ag}(\text{py-O})_2][\text{OMs}]$ contains one silver atom, coordinated to two py-O ligands and one methanesulfonate anion through one of its oxygens. All Ag-O distances vary between 2.3389(1) Å and 2.5820(1) Å (Table S1). Each py-O ligand is bidentate and connects two $[\text{Ag}(\text{py-O})_2(\text{OMs})]$ units making each silver-atom five coordinate (Figure 4). Due to the bridging py-O ligands, chains of $[\text{Ag}(\text{py-O})_2(\text{OMs})]_\infty$ are formed parallel to the crystallographic *b* axis. The π - π interactions between the py-O ligands in the asymmetric unit are presented in Table S2.

[Insert Figure 4]

Single crystals of $[\text{Ag}(\text{py-O})_2][\text{NO}_3]$ crystallized from $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$. The asymmetric unit contains one silver atom, coordinated by two py-O ligands and one nitrate anion that coordinates in a bidentate fashion. Two silver centers are connected to one another through two bidentate

bridging py-O ligands to form a $[\text{Ag}_2(\text{py-O})_4(\text{NO}_3)_2]$ moiety (Figure S7). The other py-O ligands are monodentate. Overall, each silver atom is five coordinate as shown in Figure S7. All Ag-O distances vary between 2.2958(1) Å and 2.4253(1) Å, but the distances between silver and the oxygen from the py-O ligands is shorter than the distance between silver and the oxygen of the nitrate anion (Table S1). In contrast with the previously described crystal structures there is no infinite chain structure, due to the bidentate nature of the NO_3 coordination. The $[\text{Ag}_2(\text{py-O})_4(\text{NO}_3)_2]$ -moieties are aligned in sheets parallel to the $[1\ 0\ -1]$ direction as is shown in Figure S8. For more information about the π - π interactions, see Table S2.

Thermal stability

TGA traces were measured for $[\text{Ag}(\text{py-O})_3][\text{OTf}]$, $[\text{Ag}(\text{py-O})_6][\text{OTf}]$, $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ and $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ (Figure 5). The nitrate complex started losing py-O ligands at 120 °C and it had about 37% of its mass remaining at 240 °C, corresponding to the loss of three py-O ligands and AgNO_3 remaining. At even higher temperatures, the nitrate anion degraded as well. $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ was also found to be thermally stable up to 120 °C, after which its mass started decreasing. At 400 °C, the compound with the trifluoromethanesulfonate anion had about 45% of its mass remaining, indicating that three py-O ligands had evaporated and that the residue was AgOTf . Both compounds appeared to be stable at 90 °C and electrochemical measurements were performed at this temperature. However, $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ started to degrade at temperatures as low as 50 °C. Around 250 °C, there was 41% of its initial mass remaining, corresponding to AgOMs . Above 320 °C, the methanesulfonate anion also degraded. Also $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ starts losing mass at temperatures slightly below 100 °C. This is possibly because due to the

excess of ligands, not all ligands are coordinated to the silver center and evaporate more easily. At 400 °C, about 30% of its initial mass is remaining, corresponding to a loss of 6 ligands and AgOTf remaining. To ensure comparability of the electrochemical experiments, the measurements on all compound were performed also at 90 °C, even the ones who show some small mass loss at this temperature, but care was taken to keep the compound for the shortest possible period at this elevated temperature.

[Insert Figure 5]

Electrochemistry

Cyclic voltammograms of $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$, $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ and $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ are shown in Figure 6. The cathode was a gold-sputtered silicon substrate, a silver coil was used as a sacrificial anode, and a silver wire served as pseudo reference electrode. The measurements were performed at a scan rate of 50 mV s^{-1} and a temperature of 90 °C. Since at this temperature all the tested compounds are in their liquid state, the 1:3 metal-to-ligand stoichiometry is present, independent of what crystals might form at lower temperatures. All cyclic voltammograms were measured in a custom-made PTFE sample holder with a narrow channel in front of the cathode, in order to make the current density uniform and to have a well-defined surface area.¹⁵ Over this channel, an iR drop arises. All cyclic voltammograms were corrected for this iR drop, using a current interrupt technique as described elsewhere.¹⁵ The cyclic voltammograms show the typical deposition/stripping behavior, with silver deposition at negative potentials vs. the Ag/Ag^+ pseudo-reference electrode and stripping of silver at positive potentials. At potentials more

positive than +0.7 V vs Ag/Ag⁺, oxidation of the pyridine-*N*-oxide ligands was observed. The liquid metal salts do not show a cathodic decomposition limit, since the cathodic reaction is the deposition of silver. At the anode, silver is regenerated into solution by oxidation of silver metal to silver(I) ions. Interestingly, the compounds with fluorine-free anions, [Ag(py-O)₃][NO₃] and [Ag(py-O)₃][OMs], showed the highest current densities of -10 and -6.5 A dm⁻² at -0.5 V vs Ag/Ag⁺, respectively, while the lowest current densities (-2.5 A dm⁻²) were observed for the compound with the trifluoromethanesulfonate anion, [Ag(py-O)₃][OTf]. This can be explained by differences in viscosity: the lower the viscosity of a compound, the faster the transport of silver ions through the electrolyte and the higher the current density. [Ag(py-O)₃][NO₃] has the lowest viscosity and also showed the highest current densities. The compound with trifluoromethanesulfonate anions has the highest viscosity, so the lowest current densities were observed.

[Insert Figure 6]

In agreement with earlier studies¹⁵⁻²⁰ on copper- and silver-containing liquid metal salts, no cathodic peak was observed (no limiting current), indicating that the electrochemical process never enters a diffusion-controlled regime. Therefore, the system was pushed to very negative potential values and a linear potential scan to potential values as negative as -10 V vs Ag/Ag⁺ was measured (Figure 7). [Ag(py-O)₃][NO₃] shows a remarkably high current density of -22.5 A dm⁻², while [Ag(py-O)₃][OMs] and [Ag(py-O)₃][OTf] have a current density of -16 and -9 A dm⁻².

², respectively. These results were not corrected for *iR* drop, since at high potentials this technique becomes unstable.

[Insert Figure 7]

Since silver is six coordinate in $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$, $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ and $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$, due to the bidentate bridging coordination of the py-O ligands, the liquid metal salt with a 1:6 metal-to-ligand ratio $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ was synthesized to check whether all six coordination positions of silver could be filled by monodentate py-O ligands. The result was a room temperature liquid with a low viscosity, which formed crystals of $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ submersed in an excess of py-O after standing at room temperature for a few days. To test the influence of this excess of ligands on electrochemical properties, a cyclic voltammogram of $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ was measured at 90 °C, a temperature at which the crystals were melted. The cyclic voltammogram (Figure 8) shows an overall shape equal to those in Figure 6, but the current density at -0.25 V vs Ag/Ag^+ is a factor two higher than for $[\text{Ag}(\text{py-O})_3][\text{OTf}]$. This is due to the much lower viscosity of $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ (only 8 mPa·s at 80 °C) compared to that of $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ (35 mPa·s at 80 °C). However, the current density of $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ is not as high as that of $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$, while its viscosity is lower. This is possibly due to the lower silver content of $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ (13.03 wt% Ag) versus that of $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ (23.70 wt%).

[Insert Figure 8]

Scanning electron microscopy (SEM) images were made for all silver films, deposited at -1.0 A dm^{-2} (thickness: $0.65 \text{ }\mu\text{m}$) and -5.0 A dm^{-2} (thickness: $3.22 \text{ }\mu\text{m}$) for 60 seconds (Figure 9). At higher current densities, the silver coatings were rougher for all the tested silver-containing liquid metal salts. Nonetheless, the silver deposits of all silver complexes showed a good coverage of the surface. The silver deposits of $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ at -5.0 A dm^{-2} showed the strongest tendency to grow dendritically, even though a special sample holder is used to reduce dendritic growth. EDX measurements showed that the deposits were pure silver (Figure S9). Since no gold peak was found in the EDX spectra, the surface was completely covered.

[Insert Figure 9]

Conclusion

Several new silver-containing liquid metal salts with pyridine-*N*-oxide ligands were synthesized, characterized and tested as electrolytes for silver electrodeposition. All ionic liquids showed remarkably high current densities and produced silver deposits of good quality, even without the use of additives. For the non-fluorinated liquid metal salt $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$, the highest current density of -10 A.dm^{-2} at $-0.5 \text{ V vs Ag/Ag}^+$ was observed. Crystal structures of $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$, $[\text{Ag}(\text{py-O})_3][\text{OTf}]$, $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$, $[\text{Ag}(\text{py-O})_2][\text{OMs}]$ and $[\text{Ag}(\text{py-O})_2][\text{NO}_3]$ were described and showed the variable coordination of the silver centers, the ligands and the anions. This paper shows that silver-containing ionic liquids with non-fluorinated anions can be

successfully used for the electrodeposition of high quality silver coatings. This is a significant progress compared to earlier results, because ionic liquids with non-fluorinated anions are much cheaper than their fluorinated counter parts. Moreover, no issues with fluorinated decomposition products need to be taken into account.

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Electronic Supplementary Information

Electronic supplementary information (ESI) available: crystallographic data in CIF format, additional figures of the crystal structures of α -[Ag(py-O)₃][Tf₂N], β -[Ag(py-O)₃][Tf₂N], [Ag₃(py-O)₈][OTf]₃, [Ag(py-O)₃][OTf] and [Ag(py-O)₂][NO₃] and tables with crystallographic information about interatomic distances (Table S1) and π - π interactions (Table S2).

References

- ¹ a) K. R. Seddon, *J. Chem. Technol. Biotechnol.*, **1997**, 68, 351-356; b) T. Welton, *Chem. Rev.*, **1999**, 99, 2071-2083; c) P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.*, **2000**, 39, 3772-3789; d) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.*, **2008**, 37, 123-150; e) S. A. Forsyth, J. M. Pringle, D. R. MacFarlane, *Aust. J. Chem.* **2004**, 57, 113-119.
- ² F. Endres, *ChemPhysChem*. **2002**, 3, 144-154; b) S. Zein El Abedin., F. Endres, *ChemPhysChem*. **2006**, 7, 58-61; c) A. P. Abbott, K. J. McKenzie, *Phys. Chem. Chem. Phys.* **2006**, 8, 4265, 4249; d) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, 8, 621-629.
- ³ a) K. Binnemans, *Chem. Rev.* **2007**, 107, 2592, 2614; b) S. Schaltin, P. Nockemann, B. Thijs, K. Binnemans, J. Fransaer, *Electrochem. Solid-State Lett.* **2007**, 10, D104-D107.
- ⁴ a) J. A. Welleman, F. B. Hulsbergen, J. Verbiest, J. Reedijk, *J. Inorg. Nucl. Chem.*, **1978**, 40, 143-147; b) A. C. Albeniz, J. Barbera, P. Espinet, M. C. Lequerica, A. M. Levelut, F. J. Lopez-Marcos, J. L. Serrano, *Eur. J. Inorg. Chem.*, **2000**, 133-138.
- ⁵ T. Vander Hoogerstraete, N. R. Brooks, B. Norberg, J. Wouters, K. Van Hecke, L. Van Meervelt, K. Binnemans, *CrystEngComm*, **2012**, 14, 4902-4911.
- ⁶ a) T. Mochida, Y. Funasako, T. Inagaki, M.J. Li, K. Asahara, D. Kuwahara, *Chemistry- A European Journal*, **2013**, 19, 6257-6264; b) S. Mori, T. Mochida, *Organometallics*, **2013**, 32, 3, 780-787; c) Y. Funasako, M. Nosho, T. Mochida, *Dalton Trans.*, **2013**, 42, 28, 10138-10143; d) Y. Funasako, T. Inagaki, T. Mochida, T. Sakurai, H. Ohta, K. Furukawa, T. Nakamura, *Dalton Trans.*, **2013**, 42, 8317-8327.
- ⁷ W. Wang, D. Lee, A.M. Leone, R.W. Murray, *Chem. Phys*, **2005**, 319, 1-3, 126-135.

- ⁸ a) M. Iida, C. Baba, M. Inoue, H. Yoshida, E. Taguchi, H. Furusho, *Chem. Eur. J.*, **2008**, *14*, 5047-5056; b) M. Iida, S. Kawakami, E. Syouno, H. Er, E. Taguchi, *J. Colloid Interface Sci.*, **2011**, *356*, 630-638.
- ⁹ A. P. Abbott, J. C. Barron, K. S. Ryder, D. Wilson, *Chem. Eur. J.* **2007**, *13*, 6495-6501.
- ¹⁰ A. Cingolani, Effendy, F. Marchetti, C. Pettinari, B. W. Skelton, A. H. White, *Dalton Trans.*, **1999**, 4047-4055.
- ¹¹ J. F. Huang, H. M. Luo, S. Dai, *J. Electrochem. Soc.*, **2006**, *153*, J9-J13.
- ¹² A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, *Chem. Eur. J.* **2004**, *10*, 3769-3774.
- ¹³ H. M. A. Abood, A. P. Abbott, A. D. Ballantyne, K. S. Ryder, *Chem. Commun.* **2011**, *47*, 3523-3525.
- ¹⁴ a) T. M. Anderson, D. Ingersoll, A. J. Rose, C. L. Staiger, J. C. Leonard, *Dalton Trans.*, **2000**, *39*, 8609-8612; b) H. D. Pratt, A. J. Rose, C. L. Staiger, D. Ingersoll, T. M. Anderson, *Dalton Trans.*, **2011**, *40*, 11396-11401.
- ¹⁵ S. Schaltin, N. R. Brooks, K. Binnemans, J. Fransaer, *J. Electrochem. Soc.*, **2011**, *158*, D21-D27.
- ¹⁶ S. Schaltin, N. R. Brooks, L. Stappers, L. D'Urzo, H. Plank, G. Kothleitner, C. Gspan, K. Binnemans, J. Fransaer, *J. Electrochem. Soc.*, **2011**, *158*, D647-D650.
- ¹⁷ N. R. Brooks, S. Schaltin, K. Van Hecke, L. Van Meervelt, K. Binnemans, J. Fransaer, *Chem. Eur. J.* **2011**, *17*, 5054-5059.
- ¹⁸ S. Schaltin, N. R. Brooks, L. Stappers, K. Van Hecke, L. Van Meervelt, K. Binnemans, J. Fransaer, *Phys. Chem. Chem. Phys.*, **2012**, *14*, 1706-1715.
- ¹⁹ N. R. Brooks, S. Schaltin, K. Van Hecke, L. Van Meervelt, J. Fransaer, K. Binnemans, *Dalton Trans.*, **2012**, *41*, 6902-6905.

- ²⁰ D. Depuydt, N. R. Brooks, S. Schaltin, L. Van Meervelt, J. Fransaer, K. Binnemans, *ChemPlusChem*, **2013**, 78, 578-588.
- ²¹ a) S. Kida, J. V. Quagliano, J. A. Walmsley, S. Y. Tyree, *Spectrochimica Acta*, **1968**, 56, 189-199; b) I. Rey, P. Johansson, J. Lindgren, J. C. Lassègues, J. Grondin, L. Servant, *J. Phys. Chem. A*, **1998**, 102, 3249-3258.
- ²² A. Basile, A. I. Bhatt, A. P. O'Mullane and S. K. Bhargava, *Electrochim. Acta*, **2011**, 56, 2895.
- ²³ CrysAlisPro, Agilent Technologies, Yarnton, UK, **2011**.
- ²⁴ G. M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112-122.
- ²⁵ A. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, **2009**, 42, 339.

Table 1: Melting points and viscosity of the complexes.

Compound	m.p. (°C)	Viscosity (mPa·s) (80 °C)
[Ag(py-O) ₃][Tf ₂ N]	108	n.d. ^b
[Ag(py-O) ₃][OTf]	76	35
[Ag(py-O) ₆][OTf]	< RT ^a	8
[Ag(py-O) ₃][OMs]	77	22
[Ag(py-O) ₃][NO ₃]	67	18

^a Room temperature ionic liquid, but [Ag(py-O)₃][OTf] crystallized out over time.

^b n.d.: not determined, because of high melting point.

Table 2: Crystal data and structure refinement for the structures of α -[Ag(py-O)₃][Tf₂N], β -[Ag(py-O)₃][Tf₂N], [Ag₃(py-O)₈][OTf]₃, [Ag(py-O)₃][OTf], [Ag(py-O)₂(OMs)] and [Ag(py-O)₂(NO₃)].

	[Ag(py-O) ₃][Tf ₂ N] α -polymorph	[Ag(py-O) ₃][Tf ₂ N] β -polymorph	[Ag ₃ (py-O) ₈][OTf] ₃	[Ag(py-O) ₃][OTf]	[Ag(py-O) ₂ (OMs)]	[Ag(py-O) ₂ (NO ₃)]
Empirical formula	C ₁₇ AgF ₆ N ₄ O ₇ S ₂ H ₁₅	C ₁₇ AgF ₆ N ₄ O ₇ S ₂ H ₁₅	C ₄₃ H ₄₀ Ag ₃ F ₉ N ₈ O ₁₄ S ₃	C ₁₆ H ₁₅ AgF ₃ N ₃ O ₆ S	C ₁₁ H ₁₃ AgN ₂ O ₅ S	C ₁₀ H ₁₀ AgN ₃ O ₅
Formula weight	673.32	673.32	1483.62	542.24	393.17	360.07
Temperature/K	100	100	100	100	100	100
Color	colorless	colorless	colorless	colorless	colorless	colorless
Size/mm ³	0.36×0.20×0.12	0.40×0.20×0.10	0.27×0.19×0.11	0.40×0.08×0.07	0.28×0.24×0.12	0.14×0.10×0.03
Crystal system	trigonal	rhombohedral	orthorhombic	tetragonal	orthorhombic	triclinic
Space group	<i>P</i> 31 <i>c</i> (no. 159)	<i>R</i> -3 (no. 148)	<i>P</i> 2 ₁ (no. 4)	<i>I</i> 4 ₁ / <i>a</i> (no. 88)	<i>P</i> 2 ₁ / <i>c</i> (no.14)	<i>P</i> -1 (no. 2)
<i>a</i> /Å	25.4018(11)	25.5554(4)	7.0245(2)	25.9649(5)	11.6001(2)	8.2360(4)
<i>b</i> /Å	25.4018(11)	25.5554(4)	25.8560(8)	25.9649(5)	6.90176(1)	8.7680(5)
<i>c</i> /Å	12.772(5)	56.4189(11)	14.6711(4)	11.8154(3)	17.1007(4)	8.7895(4)
α /°	90	90	90	90	90	77.874(5)
β /°	90	90	90.513(3)	90	104.866(2)	80.894(4)
γ /°	120	120	90	90	90	72.726(5)
Volume/Å ³	7028.2(5)	31909.5(9)	2665.49(2)	7965.6(3)	1323.28(4)	589.44(5)
<i>Z</i>	12	18	2	16	4	2

$\rho_{\text{calc}} \text{ Mg/m}^3$	1.909	1.892	1.908	1.809	1.973	2.029
μ/mm^{-1}	1.134	1.124	1.318	1.184	1.701	1.731
Wavelength/ $\text{\AA}$	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Reflections collected	8083	16793	9891	4888	3055	2664
Independent reflections	6650	14641	9405	4419	2809	2531
R(int)	0.0460	0.0446	0.0361	0.0265	0.0231	0.0180
R1 [$I \geq 2\sigma(I)$]	0.0324	0.0378	0.0333	0.0221	0.0201	0.0166
wR ₂ [all data]	0.0659	0.0922	0.0644	0.0544	0.0469	0.0433
$\Delta\rho_{\text{max,min}} / \text{e \AA}^{-3}$	0.736/-1.033	0.787/-0.583	0.821/-0.736	0.563/-0.445	0.426/-0.393	0.527/-0.333

Figure captions

Figure 1: View of the Ag...Ag interactions and their py-O ligands in the α -polymorph of $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$. Disorder of the anions is omitted for clarity.

Figure 2: View along the c axis of the packing in the crystal structure of a the β -polymorph of $[\text{Ag}(\text{py-O})_3][\text{Tf}_2\text{N}]$. Disorder of the anions is omitted for clarity.

Figure 3: View of the one-dimensional chain structure of the $[\text{Ag}_3(\text{py-O})_8]_\infty$ chains in the structure of $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$.

Figure 4: View of the $[\text{Ag}(\text{py-O})_2][\text{OMs}]_\infty$ chain moieties in the structure of $[\text{Ag}(\text{py-O})_2][\text{OMs}]$.

Figure 5: TGA trace of $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ (solid line), $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ (dashed line), $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ (dotted line) and $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ (dashed-dotted line) in an argon atmosphere. Heating rate: $5\text{ }^\circ\text{C min}^{-1}$.

Figure 6: Cyclic voltammogram of $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ (solid line), $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ (dashed line) and $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ (dotted line) vs Ag/Ag^+ reference electrode. Scan rate: 50 mV s^{-1} , temperature $90\text{ }^\circ\text{C}$, on a gold-sputtered silicon electrode.

Figure 7: Linear potential scan of $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ (solid line), $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ (dashed line) and $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ (dotted line) vs Ag/Ag^+ reference electrode. Scan rate: 50 mV s^{-1} , temperature $90\text{ }^\circ\text{C}$, on a gold-sputtered silicon electrode.

Figure 8: Cyclic voltammogram of $[\text{Ag}(\text{py-O})_6][\text{OTf}]$ vs Ag/Ag^+ reference electrode. Scan rate: 50 mV s^{-1} , temperature $90\text{ }^\circ\text{C}$, on a gold-sputtered silicon electrode.

Figure 9: SEM images of deposits at -1.0 A dm^{-2} from $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ (a), $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ (b) and $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ (c), and deposits at -5.0 A dm^{-2} from $[\text{Ag}(\text{py-O})_3][\text{NO}_3]$ (d), $[\text{Ag}(\text{py-O})_3][\text{OMs}]$ (e) and $[\text{Ag}(\text{py-O})_3][\text{OTf}]$ (f).

Figure 1:

Figure 2:

Figure 3:

Figure 5:

Figure 6:

Figure 7:

Figure 8:

Figure 9: