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SUPPLEMENTARY MATERIAL TO

A study on tailor made ruthenium sulphoxide complexes: Synthesis, characterization and application

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PHYSICAL, ANALYTICAL AND SPECTRAL DATA FOR THE SYNTHESISED COMPLEXES

*[{*Cis,fac-*$RuCl_2(DMSO)_3\}_2$*(μ-5,5'-methylenebis(2-aminopyridine))]·2DMSO* ***(1)***. Yield: 86.7 %; yellowish brown solid; m.p.: 112 °C; Anal. Calcd. for $C_{27}H_{60}N_4S_8O_8Cl_4Ru_2$ (FW: 1169.21): C, 27.73; H, 5.17; N, 4.79; S, 21.94 %. Found: C, 27.69; H, 5.21; N, 4.72; S, 21.88 %; IR (KBr, cm^{-1}): 3485 (N–H stretching of NH_2 group), 2860, 2830 (C–H stretching of CH_2), 1650, 1634, 1552, 1490 (C=C and C=N stretching of ring), 1281 (C–N stretching of C–NH_2), 1096, 1050 (SO stretching bands of sulphoxide), 404 (Ru–S stretching), 336, 331 (Ru–Cl stretching), 282 (Ru–N stretching); ^{1}H-NMR (400 MHz, D_2O, δ / ppm): 7.94–6.93 (6H, *m*, Ar-H); 5.46 (4H, *brs*, NH_2); 3.50 (12H, *s*, CH_3), 3.48 (12H, *s*, CH_3), 3.40 (12H, *s*, CH_3), 2.78 (12H, *s*, CH_3); 2.73 (2H, *s*, CH_2); ^{13}C{^{1}H}-NMR (400 MHz, D_2O, δ / ppm): 146.8–110.1 (Ar-C); 45.7, 45.3, 44.3, 37.8 (SC); 39.8 (CH_2); MS (*m*/*z*): 1170 $(M+H)^+$; UV–Vis (MeCN) (λ_{max} / nm (ε / mol^{-1} dm^3 cm^{-1})): 590 (100), 390 (410), 324 (550), 228 (780). Conductivity (H_2O, 25 °C, Δm / Ω^{-1} mol^{-1} dm^3 cm^{-1}): 68.

*[{*Trans,mer-*$RuCl_2(DMSO)_3\}_2$*(μ-5,5'-methylenebis(2-aminopyridine))]·2DMSO* ***(2)***. Yield: 91.2 %; golden yellow powder; m.p.: 123 °C; Anal. Calcd. for $C_{27}H_{60}N_4S_8O_8Cl_4Ru_2$ (FW: 1169.21): C, 27.73; H, 5.17; N, 4.79; S, 21.94 %. Found: C, 27.82; H, 5.20; N, 4.76; S, 21.86 %; IR (KBr, cm^{-1}): 3490 (N–H stretching of NH_2 group), 2842, 2835 (C–H stretching of CH_2), 1651, 1626, 1550, 1480 (C=C and C=N stretching of ring), 1283 (C–N stretching of C–NH_2), 1101, 1058 (SO stretching bands of sulphoxide), 402 (Ru–S stretching), 334, 330 (Ru–Cl stretching), 278 (Ru–N stretching); ^{1}H-NMR (400 MHz, D_2O, δ / ppm): 7.92–7.03 (6H, *m*, Ar-H); 5.43 (4H, *brs*, NH_2); 3.49 (12H, s, CH_3), 3.37 (24H, *s*, CH_3), 2.71 (12H, *s*, CH_3); 2.84 (2H, *s*, CH_2); ^{13}C{^{1}H}-NMR (400 MHz, D_2O,

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δ / ppm): 147.6–112.1 (Ar-C); 46.7, 44.9, 37.6 (SC); 39.4 (CH_2); MS (*m*/*z*): 1170 $(M+H)^+$; UV–Vis (MeCN) (λ_{max} / nm (ε / mol^{-1} dm^3 cm^{-1})): 630 (46), 472 (620), 360 (806), 300 (705). Conductivity (H_20, 25 °C, Δm / Ω^{-1} mol^{-1} dm^3 cm^{-1}): 52.

*$[(DMSO)_2H]_2^+[\{$*trans-*$Ru(DMSO)Cl_4\}_2$*(μ-*5,5'-methylenebis(2-aminopyridine))]$^{2-}$* ***(3)***. Yield: 91.7 %; yellow powder; m.p.: 153 °C; Anal. Calcd. for $C_{23}H_{50}N_4S_6O_6Cl_8Ru_2$ (FW: 1156.77): C, 23.88; H, 4.36; N, 4.84; S, 16.63 %. Found: C, 23.79; H, 4.34; N, 4.78; S, 16.70 %; IR (KBr, cm^{-1}): 3485 (N–H stretching of NH_2 group); 2860, 2843 (C–H stretching of CH_2), 1671, 1620, 1546, 1468 (C=C and C=N stretching of ring), 1278 (C–N stretching of C–NH_2), 1100, 1056 (SO stretching bands of sulphoxide); 730 $[(DMSO)_2H]^+$, 405 (Ru–S stretching), 337, 331 (Ru–Cl stretching), 270 (Ru–N stretching); MS (*m*/*z*): 1175 $(M+H)^+$; UV–Vis (MeCN, $\lambda_{max,}$ / nm (ε / mol^{-1} dm^3 cm^{-1})): 476 (802), 446 (960), 302 (706); Conductivity (H_2O, 25 °C, Δm / Ω^{-1} mol^{-1} dm^3 cm^{-1}): 128; Magnetic moment ($\boldsymbol{\mu}_{eff}$ / μ_B): 1.87.

*$(Na)_2^+[\{$*trans-*$Ru(DMSO)Cl_4\}_2$*(μ-*5,5'-methylenebis(2-aminopyridine))]$^{2-}$* ***(4)***. Yield: 88.2 %; yellowish green solid; m.p.: > 220 °C; Anal. Calcd. for $C_{15}H_{24}N_4S_2O_2Cl_8Na_2Ru_2$ (FW: 888.22): C, 20.28; H, 2.72; N, 6.31; S, 7.22 %. Found: C, 20.22; H, 2.68; N, 6.27; S, 7.28 %; IR (KBr, cm^{-1}): 3480 (N–H stretching of NH_2 group); 2860, 2847 (C–H stretching of CH_2), 1646, 1630, 1560, 1465 (C=C and C=N stretching of ring), 1286 (C–N stretching of C–NH_2), 1090 (SO stretching bands of sulphoxide), 399 (Ru–S stretching), 331, 327 (Ru–Cl stretching), 276 (Ru–N stretching); MS (*m*/*z*): 911 $(M+Na)^+$; UV–Vis (MeCN, λ_{max} / nm (ε / mol^{-1} dm^3 cm^{-1})): 482 (780), 442 (901), 301 (709). Conductivity (H_2O, 25 °C, Δm / Ω^{-1} mol^{-1} dm^3 cm^{-1}): 130; Magnetic moment ($\boldsymbol{\mu}_{eff}$ / / μ_B): 1.89.

*$[\{$*Cis,fac-*$RuCl_2(TMSO)_3\}_2$*(μ-*5,5'-methylenebis(2-aminopyridine))]·2TMSO* ***(5)***. Yield: 91.2 %; golden yellow powder; m.p.: 146 °C; Anal. Calcd. for $C_{43}H_{76}N_4S_8O_8Cl_4Ru_2$ (FW: 1377.50): C, 37.49; H, 5.56; N, 4.07; S, 18.62 %. Found: C, 37.53; H, 5.49; N, 4.11; S, 18.59 %; IR (KBr, cm^{-1}): 3490 (N–H stretching of NH_2 group); 2870, 2823 (C–H stretching of CH_2), 1656, 1638, 1522, 1475 (C=C and C=N stretching of ring), 1284 (C–N stretching of C–NH_2), 1120, 1028 (SO stretching bands of sulphoxide), 403 (Ru–S stretching), 334, 330 (Ru–Cl stretching), 282 (Ru–N stretching); ^{1}H-NMR (400 MHz, D_2O, δ / ppm): 7.71–7.11 (6H, *m*, Ar-H); 5.49 (4H, *brs*, NH_2); 4.01 (8H, *m*, SCH_2), 3.98 (8H, *m*, SCH_2), 3.57 (8H, *m*, SCH_2), 2.54 (8H, *m*, SCH_2); 2.99 (2H, *s*, CH_2); 2.30 (24H, *m*, $SCCH_2$), 2.19 (8H, *m*, $SCCH_2$); $^{13}C\{^1H\}$NMR (400 MHz, D_2O, δ / ppm): 146.4–115.9 (Ar-C); 57.8, 57.7, 55.6, 54.4 (SC); 39.6 (CH_2); 27.1, 26.9, 25.7, 24.1 (SC**C**); MS (*m*/*z*): 1378 $(M+H)^+$; UV–Vis (MeCN, λ_{max} / nm (ε / mol^{-1} dm^3 cm^{-1})): 580 (35), 410 (450), 326 (682), 230 (744). Conductivity (H_2O, 25 °C, Δm / Ω^{-1} mol^{-1} dm^3 cm^{-1}): 62.

*[{*Trans,mer-*RuCl$_2$(TMSO)$_3$}$_2$(*μ-5,5'-methylenebis(2-aminopyridine))]·2TMSO* (***6***). Yield: 84.5 %; golden yellow powder; m.p.: 158 °C; Anal. Calcd. for $C_{43}H_{76}N_4S_8O_8Cl_4Ru_2$ (FW: 1377.50): C, 37.49; H, 5.56; N, 4.07; S, 18.62 %. Found: C, 37.47; H, 5.60; N, 4.09; S, 18.57 %; IR (KBr, cm^{-1}): 3475 (N–H stretching of NH_2 group), 2845, 2840 (C–H stretching of CH_2), 1650, 1637, 1572, 1463 (C=C and C=N stretching of ring), 1283 (C–N stretching of C–NH_2), 1098, 1031 (SO stretching bands of sulphoxide), 407 (Ru–S stretching), 337, 331 (Ru–Cl stretching), 286 (Ru–N stretching); ^{1}H-NMR (400 MHz, D_2O, δ / ppm): 7.63–6.99 (6H, *m*, Ar-H); 5.45 (4H, *brs*, NH_2); 3.54 (8H, *m*, SCH_2), 3.51 (16H, *m*, SCH_2), 2.55 (8H, *m*, SCH_2); 2.32 (24H, *m*, $SCCH_2$), 2.21 (8H, *m*, $SCCH_2$); 2.92 (2H, *s*, CH_2); ^{13}C{^{1}H}NMR (400 MHz, D_2O, δ / ppm): 149.9–114.8 (Ar-C); 57.2, 56.3, 54.5 (SC); 40.3 (CH_2); 27.4, 26.8, 24.3 (SC**C**); MS (*m*/*z*): 1378 $(M+H)^+$; UV–Vis (MeCN, λ_{max} / nm (ε / mol^{-1} dm^3 cm^{-1})): 662 (42), 480 (502), 360 (760), 302 (880). Conductivity (H_2O, 25 °C, Δm / Ω^{-1} mol^{-1} dm^3 cm^{-1}): 68.

*[(TMSO)H]$_2^+$[{*trans-*Ru(TMSO)Cl$_4$}$_2$(*μ-5,5'-methylenebis(2-aminopyridine))]$^{2-}$* (***7***). Yield: 83.7 %; yellow red powder; m.p.: > 220 °C; Anal. Calcd. for $C_{27}H_{46}N_4S_4O_4Cl_8Ru_2$ (FW: 1104.66): C, 29.35; H, 4.20; N, 5.07; S, 11.61 %. Found: C, 29.40; H, 4.23; N, 5.11; S, 11.66 %; IR (KBr, cm^{-1}): 3495 (N–H stretching of NH_2 group), 2850, 2810 (C–H stretching of CH_2), 1641, 1631, 1550, 1482 (C=C and C=N stretching of ring), 1280 (C–N stretching of C–NH_2), 1136, 1029 (SO stretching bands of sulphoxide), 735 $[(TMSO)H]^+$, 402 (Ru–S stretching), 338, 333 (Ru–Cl stretching), 280 (Ru–N stretching); UV–Vis (MeCN, λ_{max} / nm (ε / mol^{-1} dm^3 cm^{-1})): 472 (600), 430 (780), 301 (861); MS (*m*/*z*): 1105$(M+H)^+$; Conductivity (H_2O, 25 °C, Δm / Ω^{-1} mol^{-1} dm^3 cm^{-1}): 122; Magnetic moment ($\boldsymbol{\mu}_{eff}$ / μ_B): 1.88.

THE SPECTRA AND CHEMICAL BEHAVIOR

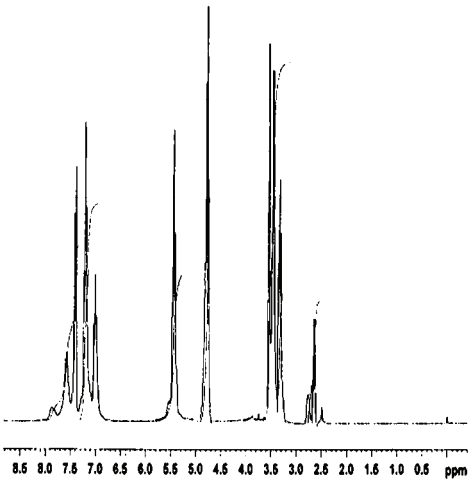

Fig. S-1. ^{1}H-NMR spectrum of **1**.

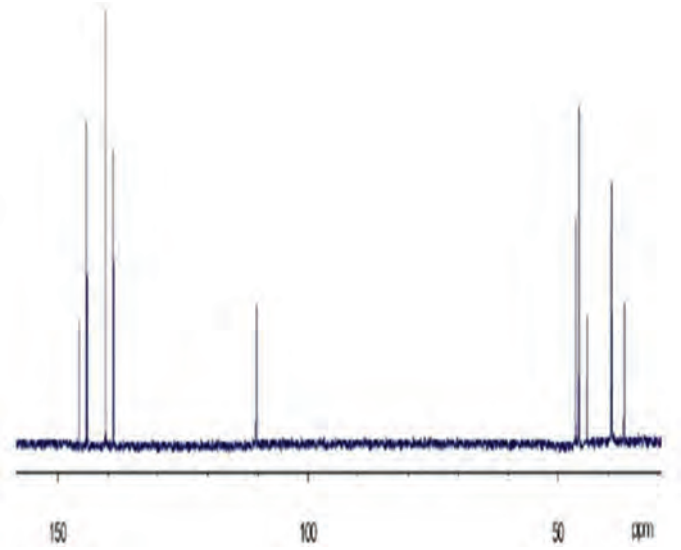

Fig. S-2. ^{13}C-NMR spectrum of **1**.

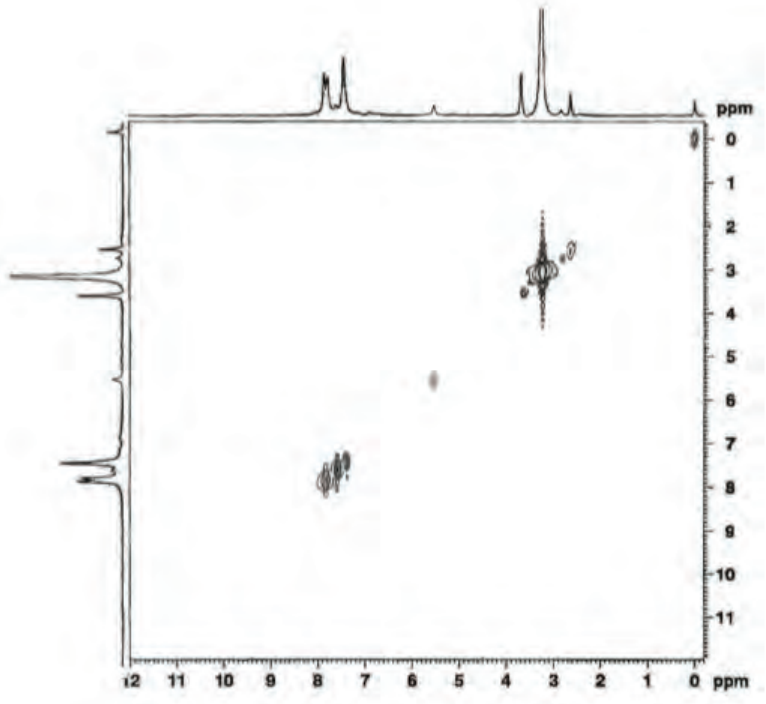

Fig. S-3. ^{1}H–^{1}H COSY NMR spectrum of **2**.

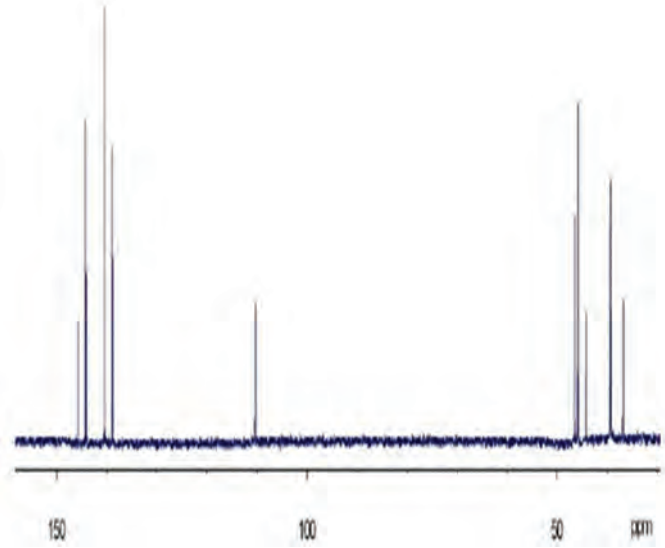

Fig. S-4. 13C-NMR spectrum of **2**.

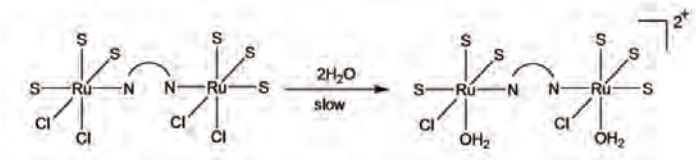

Fig. S-5. Chemical behaviour of **1** in aqueous solution.

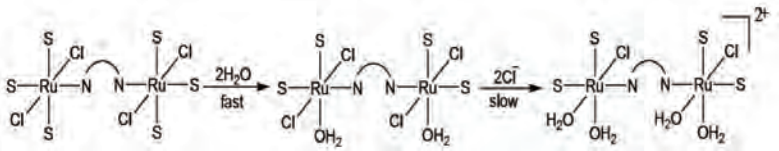

Fig. S-6. Chemical behaviour of **2** in aqueous solutions.