Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 79 (8) S98–S101 (2014) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Synthesis, characterization and cytotoxicity of mixed ligand Mn(II), Co(II) and Ni(II) complexes

SOUAD A. OSMAN[1], HANAN A. MOUSA[2], HISHAM ABDALLAH A. YOSEF[1], TAGHRID S. HAFEZ[1], ABDALLAH A. EL–SAWY[3], MOHAMED M. ABDALLAH[4] and ASHRAF S. HASSAN[1]*

[1]*Department of Organometallic and Organometalloid Chemistry, National Research Centre, El–Behoos Street, Dokki, P. O. Box 12622, Cairo, Egypt,* [2]*Department of Inorganic Chemistry, National Research Centre, El–Behoos Street, Dokki, P. O. Box 12622, Cairo, Egypt,* [3]*Chemistry Department, Faculty of Science, Benha University, Benha, Egypt and* [4]*Univet Pharmaceuticals Ltd, Balteem, Egypt*

J. Serb. Chem. Soc. 79 (8) (2014) 953–964

PHYSICAL, ANALYTIC AND SPECTRAL DATA FOR THE LIGANDS

3–(2–Phenylhydrazono)acetylacetone (HL[1]). Yield: 86 %; Yellow needles; m.p.: 86–87 °C; Anal. Calcd. for $C_{11}H_{12}N_2O_2$ (FW: 204.23): C, 64.69; H, 5.92; N, 13.72 %. Found: C, 64.50; H, 6.10; N, 13.65 %; IR (KBr, cm^{-1}): 3430–3092 (**N–H**···O=C, hydrogen bonded), 1673 (C=O, free), 1623 (C=O, hydrogen bonded), 1593 (C=N), 1518 (N–H); ^{1}H–NMR (500 MHz, DMSO–d_6, δ / ppm) 2.36 (3H, *s*, CH_3CO free), 2.43 (3H, *s*, CH_3CO hydrogen bonded), 7.16 (1H, *t*, J = 8.5 Hz, aromatic), 7.27 (2H, *t*, J = 8.5 Hz, aromatic), 7.52 (2H, *d*, J = 8.5 Hz, aromatic), 14.02 (1H, *s*, D_2O exchangeable, NH).

3–(2–(4–Chlorophenyl)hydrazono)acetylacetone (HL[2]). Yield: 86 %; Yellow needles; m.p.: 147–148 °C; Anal. Calcd. for $C_{11}H_{11}ClN_2O_2$ (FW: 238.67): C, 55.36; H, 4.65; N, 11.74 %. Found: C, 55.50; H, 4.52; N, 11.80 %; IR (KBr, cm^{-1}): 3432–3094 (**N–H**···O=C, hydrogen bonded), 1667 (C=O, free), 1625 (C=O, hydrogen bonded), 1589 (C=N), 1519 (N–H); ^{1}H–NMR (500 MHz, DMSO–d_6, δ / ppm) 2.37 (3H, *s*, CH_3CO free), 2.42 (3H, *s*, CH_3CO hydrogen bonded), 7.43 (2H, *d*, J = 8.4 Hz, aromatic), 7.57 (2H, *d*, J = 8.4 Hz, aromatic), 13.81 (1H, *s*, D_2O exchangeable, NH).

3–(2–(4–Bromophenyl)hydrazono)acetylacetone (HL[3]). Yield 86 %; Yellow needles; m.p.: 141–142 °C; Anal. Calcd. for $C_{11}H_{11}BrN_2O_2$ (FW: 283.12): C, 46.66; H, 3.92; N, 9.89 %. Found: C, 46.50; H, 4.10; N, 10.00 %; IR (KBr, cm^{-1}): 3422–3073 (**N–H**···O=C, hydrogen bonded), 1667 (C=O, free), 1623 (C=O, hydrogen bonded), 1585 (C=N), 1513 (N–H); ^{1}H–NMR (500 MHz, DMSO–d_6,

* Corresponding author. E–mail: Ashraf_salmoon@yahoo.com

δ / ppm) 2.37 (3H, *s*, CH_3CO free), 2.42 (3H, *s*, CH_3CO hydrogen bonded), 7.50 (2H, *d*, *J* = 9.15 Hz, aromatic), 7.56 (2H, *d*, *J* = 9.15 Hz, aromatic), 13.75 (1H, *s*, D_2O exchangeable, NH).

Isatin (L′). IR (KBr, cm^{-1}): 3191 (N–H), 1745 (C=O), 1731 (C=O); ^{1}H–NMR (500 MHz, DMSO–d_6, δ / ppm): 6.88 (1H, *d*, *J* = 7.7 Hz, aromatic), 7.03 (1H, *t*, *J* = 7.7 Hz, aromatic), 7.46 (1H, *d*, *J* = 7.7 Hz, aromatic), 7.54 (1H, *t*, *J* = 7.7 Hz, aromatic), 10.98 (1H, *s*, D_2O exchangeable, NH).

PHYSICAL, ANALYTIC AND SPECTRAL DATA FOR THE COMPLEXES

[NiL′L^1(OH)(H$_2$O)] (***1***). Yield 50 %; Greenish yellow; m.p.: 215–218 °C; Anal. Calcd. for $C_{19}H_{19}N_3NiO_6$ (FW: 444.06): C, 51.39; H, 4.31; N, 9.46 %. Found: C, 51.50; H, 4.25; N, 9.55 %; IR (KBr, cm^{-1}): 3522 (O–H), 3181 (N–H, L′), 1717 (C=O, L′), 1709 (C=O, L′), 1667 (C=O free, L^1), 1600 (C=O coordinated, L^1), 1590 (C=N, L^1), 583 (Ni–N), 493 (Ni–O); UV–Vis (DMSO) (λ_{max} / nm): 963, 576, 420; magnetic moment ($\boldsymbol{\mu}_{eff}$ / μ_B): 3.17; molar conductivity (DMF, *c* / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 11.6.

[CoL′L^1(OH)(H$_2$O)] (***2***). Yield 53 %; Dark green; m.p.: 209–211 °C; Anal. Calcd. for $C_{19}H_{19}CoN_3O_6$ (FW: 444.30): C, 51.36; H, 4.31; N, 9.46 %. Found: C, 51.55; H, 4.25; N, 9.55 %; IR (KBr, cm^{-1}): 3580 (O–H), 3183 (N–H, L′), 1715 (C=O, L′), 1707 (C=O, L′), 1669 (C=O free, L^1), 1602 (C=O coordinated, L^1), 1591 (C=N, L^1), 584 (Co–N), 491 (Co–O); UV–Vis (DMSO) (λ_{max} / nm): 654, 540 nm; magnetic moment ($\boldsymbol{\mu}_{eff}$ / μ_B): 4.92; molar conductivity (DMF, *c* / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 12.8.

[MnL′L^1(OH)(H$_2$O)] (***3***). Yield 45 %; Green; m.p. 210–212 °C; Anal. Calcd. for $C_{19}H_{19}MnN_3O_6$ (FW: 440.31): C, 51.83; H, 4.35; N, 9.54 %. Found: C, 51.70; H, 4.40; N, 9.47 %; IR (KBr, cm^{-1}): 3544 (O–H), 3182 (N–H, L′), 1719 (C=O, L′), 1711 (C=O, L′), 1661 (C=O free, L^1), 1605 (C=O coordinated, L^1), 1590 (C=N, L^1), 540 (Mn–N), 487 (Mn–O); UV–Vis. (DMSO) (λ_{max} / nm): 752, 618, 520 nm; magnetic moment ($\boldsymbol{\mu}_{eff}$ / μ_B): 5.82; molar conductivity (DMF, *c* / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 15.4.

[NiL′L^2(OH)(H$_2$O)] (***4***). Yield 60 %; Greenish yellow; m.p.: 217–220 °C; Anal. Calcd. for $C_{19}H_{18}ClN_3NiO_6$ (FW: 478.51): C, 47.69; H, 3.79; N, 8.78 %. Found: C, 47.50; H, 3.70; N, 8.70 %; IR (KBr, cm^{-1}): 3565 (O–H), 3180 (N–H, L′), 1715 (C=O, L′), 1707 (C=O, L′), 1661 (C=O free, L^2), 1605 (C=O coordinated, L^2), 1585 (C=N, L^2), 579 (Ni–N), 448 (Ni–O); UV–Vis (DMSO) (λ_{max} / / nm): 988, 581, 422 nm; magnetic moment ($\boldsymbol{\mu}_{eff}$ / μ_B): 3.20; molar conductivity (DMF, *c* / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 20.5.

[CoL′L^2(OH)(H$_2$O)] (***5***). Yield 58 %; Dark green; m.p.: 207–209 °C; Anal. Calcd. for $C_{19}H_{18}ClCoN_3O_6$ (FW: 478.75): C, 47.67; H, 3.79; N, 8.78 %. Found: C, 47.50; H, 3.85; N, 8.70 %; IR (KBr, cm^{-1}): 3553 (O–H), 3186 (N–H, L′), 1716 (C=O, L′), 1708 (C=O, L′), 1662 (C=O free, L^2), 1602 (C=O coordinated,

L^2), 1584 (C=N, L^2), 572 (Co–N), 438 (Co–O); UV–Vis (DMSO) (λ_{max} / nm): 661, 548 nm; magnetic moment (μ_{eff} / B.M.): 4.94; molar conductivity (DMF, c / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 22.1.

[MnL′L^2(OH)(H_2O)] (***6***). Yield 55 %; Greenish yellow; m.p.: 216–219 °C; Anal. Calcd. for $C_{19}H_{18}ClMnN_3O_6$ (FW: 474.75): C, 48.07; H, 3.82; N, 8.85 %. Found: C, 48.20; H, 3.75; N, 8.80 %; IR (KBr, cm^{-1}): 3550 (O–H), 3183 (N–H, L′), 1718 (C=O, L′), 1710 (C=O, L′), 1661 (C=O free, L^2), 1605 (C=O coordinated, L^2), 1580 (C=N, L^2), 569 (Mn–N), 444 (Mn–O); UV–Vis (DMSO) (λ_{max} / nm): 758, 622, 526 nm; magnetic moment (μ_{eff} / μ_B): 5.90; molar conductivity (DMF, c / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 19.8.

[NiL′L^3(OH)(H_2O)] (***7***). Yield 53 %; Greenish yellow; m.p.: 223–226 °C; Anal. Calcd. for $C_{19}H_{18}BrN_3NiO_6$ (FW: 522.96): C, 43.64; H, 3.47; N, 8.04 %. Found: C, 43.50; H, 3.55; N, 8.00 %; IR (KBr, cm^{-1}): 3575 (O–H), 3184 (N–H, L′), 1722 (C=O, L′), 1711 (C=O, L′), 1660 (C=O free, L^3), 1600 (C=O coordinated, L^3), 1580 (C=N, L^3), 578 (Ni–N), 447 (Ni–O); UV–Vis (DMSO) (λ_{max} / / nm): 979, 572, 420 nm; magnetic moment (μ_{eff} / μ_B): 3.19; molar conductivity (DMF, c / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 18.7.

[CoL′L^3(OH)(H_2O)] (***8***). Yield: 51 %; Greenish yellow; m.p.: 212–215 °C; Anal. Calcd. for $C_{19}H_{18}BrCoN_3O_6$ (FW: 523.20): C, 43.62; H, 3.47; N, 8.03 %. Found: C, 43.80; H, 3.40; N, 8.10 %; IR (KBr, cm^{-1}) 3535 (O–H), 3184 (N–H, L′), 1719 (C=O, L′), 1707 (C=O, L′), 1662 (C=O free, L^3), 1601 (C=O coordinated, L^3), 1582 (C=N, L^3), 584 (Co–N), 481 (Co–O); UV–Vis (λ_{max} / nm): 659, 544 nm; magnetic moment (μ_{eff} / μ_B): 4.87; molar conductivity (DMF, c / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 16.9.

[MnL′L^3(OH)(H_2O)] (***9***). Yield: 45 %; Green; m.p.: 215–218 °C; Anal. Calcd. for $C_{19}H_{18}BrMnN_3O_6$, (FW: 519.20): C, 43.95; H, 3.49; N, 8.09 %. Found: C, 44.10; H, 3.40; N, 8.15 %; IR (KBr, cm^{-1}): 3545 (O–H), 3182 (N–H, L′), 1721 (C=O, L′), 1712 (C=O, L′), 1661 (C=O free, L^3), 1602 (C=O coordinated, L^3), 1582 (C=N, L^3), 571 (Mn–N), 472 (Mn–O); UV–Vis (DMSO) (λ_{max} / nm): 755, 621, 524 nm; magnetic moment (μ_{eff} / μ_B): 5.87; molar conductivity (DMF, c / 10^{-3} mol L^{-1}, Λ_m / Ω^{-1} cm^2 mol^{-1}): 17.3.

NMR SPECTRA OF HL^2

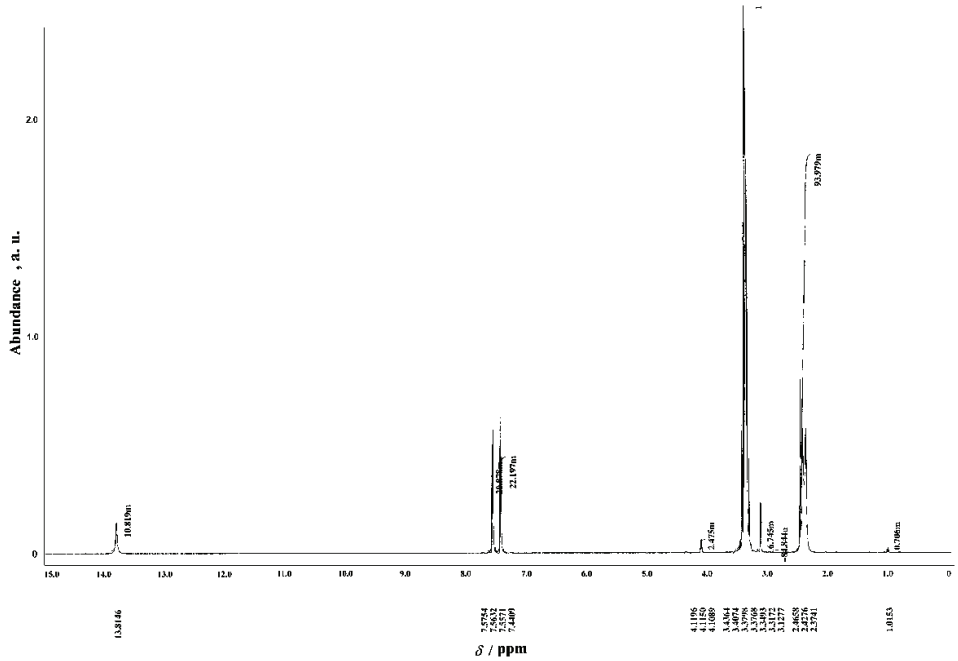

Fig. S-1. The ^{1}H-NMR spectrum of 3-(2-(4-chlorophenyl)hydrazono)acetylacetone (HL^2).