Electronic Supplementary Information (ESI) for:

Push-pull unsymmetrical substitution in nickel(II) complexes with tetradentate N_2O_2 Schiff base ligands: synthesis, structures and linear-nonlinear optical studies

Luca Rigamonti, Alessandra Forni, Stefania Righetto and Alessandro Pasini

Index

Experimental section (cont.)

Synthetic procedures for compounds 1

[Ni(^{Br}sal)$_2$(H$_2$O)$_2$] (1b).[1,2] This yellow solid was synthesized as **1a** from 5-Br-salH (281.7 mg, 1.40 mmol), ethanolic KOH (14.0 mL of a 0.1 mol L^{-1} solution, 1.40 mmol) and solid $Ni(AcO)_2{\cdot}4H_2O$ (174.2 mg, 0.70 mmol) (306.8 mg, 89%). Anal. Calcd (%) for $C_{14}H_{12}Br_2NiO_6$ (494.74): C, 33.99; H, 2.44. Found: C, 34.09; H, 2.60. IR (KBr): 3445 ($\nu_{O–H}$), 2906 (ν_{CHO}), 1631 ($\nu_{C=O}$) cm^{-1}. UV-vis ($CHCl_3$): 25060 (4130), 28650 (4620).

[Ni(^{H}sal)$_2$(H$_2$O)$_2$] (1c).[1–4] This light green solid was synthesized as above from salH (1220.4 mg, 10.00 mmol), ethanolic KOH (20.0 mL of a 0.5 mol L^{-1} solution, 10.00 mmol) and solid $Ni(AcO)_2{\cdot}4H_2O$ (1242.6 mg, 5.00 mmol) (1552.0 mg, 92%). Anal. Calcd (%) for $C_{14}H_{14}NiO_6{\cdot}0.25H_2O$ (341.46): C, 49.25; H, 4.28. Found: C, 49.41; H, 4.58. IR (KBr): 3452 ($\nu_{O–H}$), 2790 (ν_{CHO}), 1653 ($\nu_{C=O}$) cm^{-1}. UV-vis ($CHCl_3$): 25910 (3280), 30210 (5510).

[Ni(^{Me}sal)$_2$(H$_2$O)$_2$] (1d). This yellow-green compound was synthesized as above from 5-Me-salH (500.2 mg, 3.68 mmol), ethanolic KOH (7.4 mL of a 0.5 mol L^{-1} solution, 3.70 mmol) and $Ni(AcO)_2{\cdot}4H_2O$ (456.9 mg, 1.84 mmol) (518.6 mg, 77%). Anal. Calcd (%) for $C_{16}H_{18}NiO_6{\cdot}0.5H_2O$ (374.01): C, 51.38; H, 5.12. Found: C, 50.92; H, 4.93. IR (KBr): 3456 ($\nu_{O–H}$), 1633 ($\nu_{C=O}$) cm^{-1}. UV-vis ($CHCl_3$): 25060 (2300), 28990 (5620).

[Ni(5-OMe-sal)$_2$(H$_2$O)$_2$] (1e). This yellow-green compound was synthesized as above from 5-OMe-salH (500.0 μL, 4.00 mmol), ethanolic KOH (8 mL of a 0.5 mol L^{-1} solution, 4.00 mmol) and $Ni(AcO)_2{\cdot}4H_2O$ (497.6 mg, 2.00 mmol) (364.0 mg, 46%). Anal. Calcd (%) for $C_{16}H_{18}NiO_8$ (397.00): C, 48.41; H, 4.57. Found: C, 48.39; H, 4.55. IR (KBr): 3457 ($\nu_{O–H}$), 2787 (ν_{CHO}), 1659 ($\nu_{C=O}$) cm^{-1}. UV-vis ($CHCl_3$): 23700 sh (2550), 27100 (6830).

Synthetic procedures for compounds 2

[Ni(^{Br}L)$_2$] (2b).[5] 5-Br-salH (214.2 mg, 1.07 mmol) was dissolved in ethanolic KOH (10.7 mL of a 0.1 mol L^{-1} solution, 1.07 mmol) and $Ni(AcO)_2{\cdot}4H_2O$ (132.2 mg, 0.53 mmol) was added under stirring, with the formation of a green precipitate. The slurry was refluxed for 1 h, then tn (134 μL, 1.61 mmol) was added, with the formation of a brown solution and after few minutes of a yellow precipitate. The mixture was refluxed for 3 h, cooled with an ice bath, and **2b** was recovered by filtration as brownish-yellow solid, washed with EtOH, $^{i}Pr_2O$ and dried under vacuum (225.3 mg, 87%). Anal. Calcd (%) for $C_{20}H_{24}Br_2N_4NiO_2$ (570.93): C, 42.07; H, 4.24; N, 9.81. Found: C, 42.41; H, 4.37; N, 9.63. MS (ESI): *m/z* 571 ($[M + H]^+$, 25%), 593 ($[M + Na]^+$, 15), 885 ([M + Ni(^{Br}L)]$^+$, 80), 1165 ($[2M + Na]^+$, 100). UV-vis: 26110 (7490). IR (KBr): 3326, 3257 (ν_{NH2}), 1627 ($\nu_{C=N}$).

[Ni(^{H}L)$_2$] (2c).[6] salH (1.50 mL, 20.40 mmol) was dissolved in ethanolic KOH (40.8 mL of a 0.5 mol L^{-1} solution, 20.40 mmol) and Ni(AcO)$_2$·4H$_2$O (2540.0 mg, 10.20 mmol) was added under stirring. The yellow mixture was stirred at 70 °C for 1 h, with the formation of a light green precipitate, and then tn (2.1 mL, 25.20 mmol) was added. The brown solution was refluxed for 3 h. The mixture was cooled with an ice bath, and **2c** was recovered by filtration as pale yellow solid, washed with EtOH, acetone and dried under vacuum (2640.0 mg, 61%). Anal. Calcd (%) for $C_{20}H_{26}N_4NiO_2$·0.5H$_2$O (422.15): C, 56.90; H, 6.45; N, 13.27. Found: C, 56.51; H, 6.47; N, 13.07. MS (ESI): *m/z* 235 ([Ni(^{H}L)]$^+$, 45%), 267 ([Ni(^{H}L)(MeOH)]$^+$, 100), 413 ([M + H]$^+$, 25), 435 ([M + Na]$^+$, 25), 647 ([M + Ni(^{H}L)]$^+$, 30). IR (KBr): 3456 (ν_{O-H}), 3326, 3255 (ν_{NH2}), 1629 ($\nu_{C=N}$) cm^{-1}. UV-vis: 27250 (7450).

[Ni(^{Me}L)$_2$] (2d). 5-Me-salH (408.3 mg, 3.00 mmol) was dissolved in ethanolic KOH (6.0 mL of a 0.5 mol L^{-1} solution, 3.00 mmol) and Ni(AcO)$_2$·4H$_2$O (373.3 mg, 1.50 mmol) was added under stirring. The reaction mixture was refluxed for 1 h, then tn (335 µL, 4.00 mmol) was added with the formation of a brown solution, which was refluxed for 3 h. The dark brown solution was left at slow evaporation for few days, yielding **2d** as light green solid that filtered, washed with EtOH, ^{i}Pr$_2$O and dried under vacuum. Further product was recovered treating the reaction solution with water (691.1 mg, 92%). Anal. Calcd (%) for $C_{22}H_{30}N_4NiO_2$·0.5EtOH·2H$_2$O (500.26): C, 55.22; H, 7.45; N, 11.20. Found: C, 55.09; H, 7.43; N, 11.10. MS (ESI): *m/z* 249 ([Ni(^{Me}L)]$^+$, 20%), 267 ([Ni(^{Me}L)(H$_2$O)]$^+$, 100), 441 ([M + H]$^+$, 10), 463 ([M + Na]$^+$, 20), 689 ([M + Ni(^{Me}L)]$^+$, 40). IR (KBr): 3449 (ν_{O-H}), 3317, 3276 (ν_{NH2}), 1639 ($\nu_{C=N}$) cm^{-1}. UV-vis: 26180 (7240).

Synthetic procedures for compounds 3 and 4

[Ni(5'-OMe-saltn)] (3c). ***First method 1e + 2c***: **1e** (172.5 mg, 0.43 mmol) and **2c** (172.5 mg, 0.43 mmol) were dissolved in EtOH (30 mL) and refluxed for 5 h. The mixture was cooled with an ice bath and **3c** was filtered as green solid, washed with cold EtOH, ^{i}Pr$_2$O and dried under vacuum (231.0 mg, 68%). Anal. Calcd for $C_{18}H_{18}N_2NiO_3$·1.5H$_2$O (396.06): C, 54.59; H, 5.34; N, 7.07. Found: C, 54.65; H, 5.22; N, 6.81. MS (ESI): *m/z* 369 ([M + 1]$^+$, 100%), 737 ([2M + 1]$^+$, 20), 759 ([2M + Na]$^+$, 25). IR (KBr): 3457 (ν_{O-H}), 1626 ($\nu_{C=N}$). ^{1}H NMR (CDCl$_3$, 298 K, 400 MHz): δ 1.31 (3H, H$_2$O), 1.89 (2H, tn central CH$_2$), 3.55 (4H, tn lateral CH$_2$), 3.74 (3H, OMe), 6.5–7.2 (9H, aromatic and N=CH) ppm.

[Ni(5,5'-Br$_2$-saltn)] (3d). This compound was synthesized with a modification of literature procedures.[7,8] 5-Br-salH (200.0 mg, 0.99 mmol) and tn (42 µL, 0.50 mmol) were dissolved in EtOH (15 mL) and the yellow mixture was refluxed for 30 minutes. NiCl$_2$·6H$_2$O (122.3 mg, 0.51 mmol) and Et$_3$N (1 mL) were then added and the mixture was refluxed for 4 h. The green solid was filtered, washed with EtOH, $^{i}Pr_2O$ and dried under vacuum (186.6 mg, 70%). Anal. Calcd (%) for $C_{17}H_{14}Br_2N_2NiO_2{\cdot}2H_2O$ (532.84): C, 38.32; H, 3.40; N, 5.26. Found: C, 37.97; H, 3.42; N, 5.27. MS (ESI): *m/z* 497 ([M + 1]$^+$, 100%). IR (KBr): 3454 ($\nu_{O–H}$), 1626 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR: not soluble.

[Ni(5-Br-saltn)] (3e) and isolation of the intermediates [$Ni_2(\mu\text{-}^{Br}L)_2(^{H}sal)_2$] (4e) and [$Ni_2(\mu\text{-}^{H}L)(^{Br}sal)_2$] (4e'). ***First method 1c + 2b***: **1c** (55.3 mg, 0.16 mmol) and **2b** (93.8 mg, 0.16 mmol) were suspended in EtOH (10 mL) and refluxed for 12 h. The intermediate **4e** was filtered as light green solid, washed with EtOH, $^{i}Pr_2O$ and dried under vacuum (117.0 mg, 80%). Anal. Calcd (%) for $C_{34}H_{34}Br_2N_4Ni_2O_6$ (871.85): C, 46.84; H, 3.93; N, 6.43. Found: C, 47.17; H, 4.10; N, 6.13. MS (ESI): *m/z* 313 ([Ni(^{Br}L)]$^+$, 10%), 356 ([Ni(^{Br}L)(MeOH)]$^+$, 100). IR (KBr): 3342, 3293 (ν_{NH2}), 1652 sh, 1631 ($\nu_{C=N}$) cm^{-1}. Further refluxing in EtOH or drying under vacuum of **4e** did not yield **3e**. ***Second method 1b + 2c***: **1b** (125.7 mg, 0.30 mmol) and **2c** (150.4 mg, 0.30 mmol) were suspended in EtOH (30 mL) and refluxed for 12 h, yielding **4e'** as light green solid (138.1 mg, 49%). Anal. Calcd (%) for $C_{34}H_{34}Br_2N_4Ni_2O_6{\cdot}2H_2O$ (907.88): C, 44.98; H, 4.22; N, 6.17. Found: C, 45.15; H, 4.42; N, 5.93. MS (ESI): *m/z* 235 ([Ni(^{H}L)]$^+$, 100%), 267 ([Ni(^{H}L)(MeOH)]$^+$, 70). IR (KBr): 3349, 3293 (ν_{NH2}), 1638 ($\nu_{C=N}$) cm^{-1}. **4e'** (135.1 mg, 0.15 mmol) was dissolved in EtOH (10 mL) and DMF (5 mL) and the brown solution was left under reflux for 3 h, after which $^{i}Pr_2O$ (20 mL) was added and the mixture was left at slow evaporation. After two days **3e** precipitated as dark green solid that was recovered by filtration, washed with $^{i}Pr_2O$ and dried under vacuum (70.6 mg, 54%). Anal. Calcd (%) for $C_{17}H_{15}BrN_2NiO_2{\cdot}H_2O$ (440.43): C, 46.84; H, 3.93; N, 6.43. Found: C, 46.61; H, 4.02; N, 5.98. MS (ESI): *m/z* 419 ([M + 1]$^+$, 100%), 859 ([2M + Na]$^+$, 20). IR (KBr): 3447 ($\nu_{O–H}$), 1624 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ 1.11 (2H, H_2O), 1.84 (2H, tn central CH_2), 3.54 (4H, tn lateral CH_2), 5.8–7.8 (9H, aromatic and N=CH) ppm.

[Ni(5-Br-5'-Me-saltn)] (3f) and isolation of the intermediate [$Ni_2(\mu\text{-}^{Br}L)_2(^{Me}sal)_2$] (4f). ***First method 1d + 2b***: **1d** (109.5 mg, 0.30 mmol) and **2b** (171.3 mg, 0.30 mmol) were suspended in EtOH (20 mL) and refluxed for 12 h, yielding the intermediate **4f** as light green solid (217.1 mg, 75%). Anal. Calcd (%) for $C_{36}H_{38}Br_2N_4Ni_2O_6{\cdot}0.5H_2O$ (908.91): C, 47.57; H, 4.32; N, 6.16. Found: C, 47.51; H, 4.20; N, 5.87. IR (KBr): 3451 ($\nu_{O–H}$), 3339, 3290 (ν_{NH2}), 1631 ($\nu_{C=N}$). The light green solid **4f** was dried under vacuum for several days, and the color changed to military green. The solid was then suspended in $^{i}Pr_2O$, filtered and dried under vacuum yielding **3f** as military green solid (177.6 mg, 67%). Anal. Calcd (%) for $C_{18}H_{17}BrN_2NiO_2$ (431.94): C, 50.05; H, 3.97; N, 6.49. Found: C, 50.03; H, 4.15; N, 6.51. MS (ESI): *m/z* 433 ([M + 1]$^+$, 100%). IR (KBr): 1624 ($\nu_{C=N}$) cm^{-1}. ***Second method 1b + 2d***: **1b** (155.5 mg, 0.31 mmol) and **2d** (154.4 mg, 0.31 mmol) were suspended in EtOH (20 mL) and refluxed for 12 h, yielding directly **3f** as green solid (228.8 mg, 82%). Anal. Calcd (%) for $C_{18}H_{17}BrN_2NiO_2·H_2O$ (449.95): C, 48.05; H, 4.26; N, 6.23. Found: C, 47.74; H, 4.19; N, 5.89. MS (ESI): *m/z* 433 ([M + 1]$^+$, 90%), 863 ([2M + 1]$^+$, 100), 885 ([2M + Na]$^+$, 50). IR (KBr): 3439 ($\nu_{O–H}$), 1626 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ 0.90 (2H, H_2O), 1.81 (2H, tn central CH_2), 2.30 (3H, Me), 3.52 (4H, tn lateral CH_2), 6.8–7.2 (8H, aromatic and N=CH) ppm.

[Ni(5-Br-5'-OMe-saltn)] (3g) and isolation of the intermediate [Ni$_2$(μ-^{Br}L)$_2$(^{OMe}sal)$_2$] (4g). ***First method 1e + 2b***: **1e** (119.1 mg, 0.30 mmol) and **2b** (171.3 mg, 0.30 mmol) were suspended in EtOH (30 mL) and refluxed for 12 h. The green solid **4g** was filtered and dried under vacuum (196.7 mg, 67%). Anal. Calcd (%) for $C_{36}H_{38}Br_2N_4Ni_2O_8·H_2O$ (931.90): C, 46.40; H, 4.11; N, 6.01. Found: C, 46.64; H, 4.11; N, 5.84. MS (ESI): *m/z* 346 ([Ni(^{Br}L)(MeOH)]$^+$, 100%). IR (KBr): 3444 ($\nu_{O–H}$), 3341, 3290 (ν_{NH2}), 1637 ($\nu_{C=N}$) cm^{-1}. The product **3g** precipitated as brown solid from the remaining reaction mixture, left for one day at room temperature, or refluxing the intermediate **4g** in EtOH for further 24 h (111.2 mg, 37%). Anal. Calcd (%) for $C_{18}H_{17}BrN_2NiO_3$ (447.94): C, 48.26; H, 3.83; N, 6.25. Found: C, 48.47; H, 3.79; N, 5.95. MS (ESI): *m/z* 449 ([M + 1]$^+$, 100%). IR (KBr): 1612, 1597 ($\nu_{C=N}$) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ 1.90 (2H, tn central CH_2), 3.74 (3H, OMe), 3.81+3.83 (4H, tn lateral CH_2), 6.5–7.5 (8H, aromatic and N=CH) ppm. Crystals suitable for X-ray diffraction were obtained by slow diffusion of ^{i}Pr$_2$O into an EtOH solution of the title compound.

[Ni(5,5'-(NO$_2$)$_2$-saltn)] (3h). This compound was synthesized with a modification of literature procedures.[7,8] 5-NO$_2$-salH (168.3 mg, 1.01 mmol) and tn (43 μL, 0.51 mmol) were dissolved in EtOH (15 mL) and the yellow mixture was refluxed for 30 minutes. $NiCl_2·6H_2O$ (121.9 mg, 0.51 mmol) and Et_3N (1 mL) were then added and the mixture was refluxed for 4 h. The green solid was filtered, washed with EtOH, ^{i}Pr$_2$O and dried under vacuum (193.0 mg, 80%). Anal. Calcd (%) for $C_{17}H_{14}N_4NiO_6·2.5H_2O$ (474.05): C, 43.07; H, 4.04; N, 11.82. Found: C, 42.82; H, 3.76; N, 11.72. MS (ESI): *m/z* 429 ([M + 1]$^+$, 100%). IR (KBr): 3454 ($\nu_{O–H}$), 1634 ($\nu_{C=N}$), 1308 (ν_{NO2}) cm^{-1}. ^{1}H NMR: not soluble.

[Ni(5-NO$_2$-5'-Br-saltn)] (3i). ***First method 1a + 2b***: **1a** (170.9 mg, 0.30 mmol) and **2b** (128.2 mg, 0.30 mmol) were suspended in EtOH (30 mL) and refluxed for 5 h. The green product **3i** was filtered, washed with EtOH, ^{i}Pr$_2$O and dried under vacuum (238.3 mg, 82%). Anal. Calcd (%) for $C_{17}H_{14}BrN_3NiO_4·H_2O$ (480.92): C, 42.46; H, 3.35; N, 8.74. Found: C, 42.42; H, 3.38; N, 8.73. MS (ESI): *m/z* 464 ([M + 1]$^+$, 50%), 949 ([2M + Na]$^+$, 100). IR (KBr): 3438 ($\nu_{O–H}$), 1650, 1627 ($\nu_{C=N}$), 1308 (ν_{NO2}) cm^{-1}. ***Second method 1b + 2a***: **1b** (152.4 mg, 0.30 mmol) and **2a** (155.3 mg, 0.30 mmol) were suspended in EtOH (30 mL) and refluxed for 5 h. The green product **3i** was filtered, washed with EtOH, ^{i}Pr$_2$O and dried under vacuum (184.5 mg, 64%). Anal. Calcd (%) for

$C_{17}H_{14}BrN_3NiO_4{\cdot}H_2O$ (480.93): C, 42.46; H, 3.35; N, 8.74. Found: C, 42.62; H, 3.48; N, 8.67. MS (ESI): *m/z* 486 ($[M + Na]^+$, 50%), 949 ($[2M + Na]^+$, 100). IR (KBr): 3439 ($\nu_{O–H}$), 1650, 1627 ($\nu_{C=N}$), 1308 (ν_{NO2}) cm^{-1}. ^1H NMR: not soluble.

[Ni(5-NO$_2$-saltn)] (3j). ***First method 1c + 2a***: **1c** (152.2 mg, 0.45 mmol) and **2a** (171.8 mg, 0.45 mmol) were suspended in EtOH (50 mL) and refluxed for 5 h. The light brown solid **3j** was filtered, washed with EtOH, $^iPr_2O$ and dried under vacuum (230.1 mg, 66%). Anal. Calcd (%) for $C_{17}H_{15}N_3NiO_4{\cdot}0.5H_2O$ (393.02): C, 51.95; H, 4.10; N, 10.69. Found: C, 52.26; H, 4.46; N, 10.33. MS (ESI): *m/z* 384 ($[M + 1]^+$, 100%), 406 ($[M + Na]^+$, 25), 789 ($[2M + Na]^+$, 90). IR (KBr): 3447 ($\nu_{O–H}$), 1624, 1599 ($\nu_{C=N}$), 1308 (ν_{NO2}) cm^{-1}. Crystals suitable for X-ray diffraction were obtained by slow diffusion of $^iPr_2O$ into a $CHCl_3$ solution of the title compound. ***Second method 1a + 2c***: **1a** (127.9 mg, 0.30 mmol) and **2c** (122.7 mg, 0.30 mmol) were suspended in EtOH (30 mL) and refluxed for 5 h. The brown solid **3j** was filtered, washed with EtOH, $^iPr_2O$ and dried under vacuum (135.7 mg, 55%). Anal. Calcd (%) for $C_{17}H_{15}N_3NiO_4{\cdot}1.5H_2O$ (411.04): C, 49.68; H, 4.41; N, 10.22. Found: C, 49.59; H, 4.14; N, 10.17. IR (KBr): 3446 ($\nu_{O–H}$), 1624, 1599 ($\nu_{C=N}$), 1308 (ν_{NO2}) cm^{-1}. ^1H NMR ($CDCl_3$, 298 K, 400 MHz): δ 1.54 (3H, H_2O), 1.99 (2H, tn central CH_2), 3.62+3.66 (4H, tn lateral CH_2), 6.6–8.1 (9H, aromatic and N=CH) ppm.

[Ni(5-NO$_2$-5’-Me-saltn)] (3k). ***First method 1d + 2a***: **1d** (109.5 mg, 0.30 mmol) and **2a** (150.9 mg, 0.30 mmol) were suspended in EtOH (30 mL) and refluxed for 7 days, yielding the product **3k** as yellow-earth solid, washed with EtOH, $^iPr_2O$ and dried under vacuum (134.5 mg, 50%). Anal. Calcd (%) for $C_{18}H_{17}N_3NiO_4{\cdot}3H_2O$ (452.09): C, 47.82; H, 5.13; N, 9.29. Found: C, 48.05; H, 4.97; N, 9.30. MS (ESI): *m/z* 398 ($[M + 1]^+$, 100%), 817 ($[2M + Na]^+$, 60). IR (KBr): 3446 ($\nu_{O–H}$), 1628, 1597 ($\nu_{C=N}$), 1309 (ν_{NO2}) cm^{-1}. The reaction was monitored by infrared spectroscopy, where it was clearly visible the disappearance of **2a** (NH_2 bands around 3200 cm^{-1}, C=N band at 1640 cm^{-1}) and the appearance of the new C=N stretching at 1628 cm^{-1} of **3k** (the formation of the hypothetic intermediate **4k** was never detected). ***Second method 1a + 2d***: **1a** (76.4 mg, 0.18 mmol) and **2d** (84.6 mg, 0.18 mmol) were suspended in EtOH (15 mL) and refluxed for 5 h. The product **3k** was filtered as yellow-earth solid, washed with EtOH, $^iPr_2O$ and dried under vacuum (114.5 mg, 85%). Anal. Calcd (%) for $C_{18}H_{17}N_3NiO_4{\cdot}H_2O$ (416.05): C, 51.96; H, 4.60; N, 10.10. Found: C, 51.92; H, 4.85; N, 10.35. MS (ESI): *m/z* 398 ($[M + 1]^+$, 100%). IR (KBr): 3445 ($\nu_{O–H}$), 1629, 1598 ($\nu_{C=N}$), 1308 (ν_{NO2}) cm^{-1}. ^1H NMR: not soluble

Table S1 Crystallographic and data collection parameters for **3c**·$CHCl_3$, **3g**·EtOH and **3j**.

	3c·$CHCl_3$	**3g**·EtOH	**3j**
Crystal Data			
Moiety formula	$C_{18}H_{18}N_2NiO_3{\cdot}CHCl_3$	$C_{18}H_{17}BrN_2NiO_3{\cdot}C_2H_6O$	$C_{17}H_{15}N_3NiO_4$
M	488.42	494.02	384.03
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*–1 (n. 2)	$P2_1/c$ (n. 14)	$P2_1/c$ (n. 14)
a / Å	10.0155(8)	10.5470(11)	10.9731(6)
b / Å	10.1973(8)	9.3472(10)	10.7934(6)
c / Å	11.2392(11)	20.660(2)	13.7310(8)
α / °	100.5860(10)	90	90
β / °	97.6650(10)	98.9680(10)	95.6060(10)
γ / °	113.6250(10)	90	90
V / Å^3, Z, Z'	1006.09(15), 2, 1	2011.9(4), 4, 1	1618.48(16), 4, 1
Reflns for cell determination	5836	4058	6997
2θ / ° for cell determination	4.5–63.5	4.8–40.8	4.5–62.0
D_x / Mg m^{-3}	1.612	1.631	1.576
μ / mm^{-1}	1.386	2.979	1.227
Colour, habit	brown, prism	brown, plate	red, rectangular prism
Dimensions / mm	0.70 × 0.38 × 0.25	0.29 × 0.16 × 0.03	0.35 × 0.33 × 0.20
Data Collection			
Temperature / K	291(2)	291(2)	293(2)
radiation λ / Å	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Scan type	φ and ω	φ and ω	φ and ω
$2\theta_{max}$ / °	65.1	55.0	60.0
h range	$-14 \rightarrow 15$	$-13 \rightarrow 13$	$-15 \rightarrow 15$
k range	$-15 \rightarrow 15$	$-12 \rightarrow 12$	$-15 \rightarrow 15$
l range	$-16 \rightarrow 17$	$-26 \rightarrow 26$	$-19 \rightarrow 19$
Intensity decay	None	None	None
Measured reflections	21696	28896	30966
Independent reflections	6864	4614	4717
Reflections with $I>2\sigma(I)$	5915	2787	4090
R_{int}	0.018	0.055	0.019
Refinement on F^2			
$R[F^2>2\sigma(F^2)]$, $wR[F^2>2\sigma(F^2)]$	0.0355, 0.1015	0.0544, 0.1443	0.0255, 0.0680
S	1.038	1.039	1.045
Parameters, restraints	254, 0	273, 1	226, 0
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.550, –0.612	0.769, –0.905	0.356, –0.202

Table S2 Computed excitation energies (λ_{max} in nm), oscillator strengths (f), difference between excited and ground state dipole moment ($\Delta\mu_{eg}$, in D), when available, and analysis of the most important contributions to the transitions for compounds **3** and selected analogue copper(II) complexes **Cu3a** and **Cu3l**.[a]

	A	D	λ_{max}, $\Delta\mu_{eg}$	f	assignment	λ_{max}, $\Delta\mu_{eg}$	f	assignment	λ_{max}, $\Delta\mu_{eg}$	f	assignment
3a	H	H	401	0.023	H → L (84%)[b]	349	0.032	H–1 → L (84%)	329	0.034	H–1 → L+1 (94%)
			381	0.064	H → L+1 (92%)						
3b	H	Me	406	0.027	H → L (85%)[b]	352	0.025	H–1 → L (82%)	335	0.043	H–1 → L+1 (94%)
			387	0.059	H → L +1 (92%)						
3c	H	OMe	424, –1.41	0.043	H → L (88%)[b]	362, –0.52	0.015	H–1 → L (67%)	346, –1.40	0.020	H → L+2 (38%)
			399, 7.12	0.043	H → L+1 (93%)				343, 2.36	0.050	H–1 → L+1 (93%)
3d	Br	Br	413	0.028	H → L (84%)[b]	364	0.030	H–1 → L (87%)	343	0.029	H–1 → L+1 (96%)
			393	0.062	H → L+1 (92%)						
3e	Br	H	403	0.014	H → L (78%)[b]	351	0.033	H–1 → L (73%)	342	0.029	H–1 → L+1 (86%)
			391	0.075	H → L+1 (83%)						
3f	Br	Me	409	0.013	H → L (87%)[b]	354	0.029	H–1 → L (68%)	348	0.033	H–1 → L+1 (86%)
			397	0.073	H → L+1 (89%)				337	0.011	H → L+2 (49%)
3g	Br	OMe	425	0.024	H → L (85%)[b]	365	0.017	H–1 → L (68%)	357	0.050	H–1 → L+1 (87%)
			413	0.060	H → L+1 (90%)				349	0.017	H → L+2 (32%)
3h	NO_2	NO_2	383	0.072	H → L (84%)[b]	336	0.024	H–1 → L (78%)	329	0.467	H → L+2 (52%)
			364	0.088	H → L+1 (85%)				323	0.022	H → L+3 (40%)
									318	0.017	H → L+4 (36%)
									314	0.031	H–1 → L+1 (52%)
3i	NO_2	Br	403	0.041	H → L (79%)[b]	349	0.074	H → L+2 (75%)	335	0.061	H–1 → L+1 (42%),
			387	0.066	H → L+1 (76%)	346	0.067	H → L+3 (37%),			H–1 → L (30%)
								H–1 → L (31%)			
3j	NO_2	H	394, 5.39	0.032	H → L (66%)[b]	350, 19.94	0.110	H → L+2 (77%)	333, 6.12	0.052	H–1 → L (56%)
			382, 1.24	0.076	H → L+1 (78%)	339, 3.34	0.035	H → L+3 (35%),			
								H–1 → L (25%)			
3k	NO_2	Me	404	0.031	H → L (67%)[b]	362	0.074	H → L+2 (75%)	338	0.081	H–1 → L (73%)
			392	0.068	H → L+1 (81%)	348	0.030	H → L+3 (50%),			

								H–1 → L (9%)			
3l	NO_2	OMe	424	0.029	H → L (68%)[b]	381	0.041	H → L+2 (76%)	343	0.108	H–1 → L (79%)
			413	0.063	H → L+1 (79%)	366	0.025	H → L+3 (59%)			
Cu3a	H	H	411	0.043	H → L (73%)[b,c]						
Cu3l	NO_2	OMe	498	0.014	H → L (46%),[b,c] H–1 → L (35%)						

[a] Calculations performed at (TD)PBE0/6-311++G(d,p) level of theory. Unrestricted formalism used for copper(II) complexes. Only transitions with f > 0.010 are reported. [b] H = HOMO, L = LUMO. Main atomic contributions to H, L and L+1: **3a**, H = 0.12 p_{O1}, 0.12 p_{O2}, 0.11 d_{Ni}; L = 0.30 p_{C17}, 0.15 p_{N2}, 0.12 p_{C13}, 0.10 p_{C15}; L+1 = 0.31 p_{C4}, 0.16 p_{N2}, 0.15 p_{C8}, 0.11 p_{C6}. **3b**, H = 0.14 p_{O2}, 0.12 p_{C16}, 0.10 d_{Ni}; L = 0.30 p_{C17}, 0.14 p_{N2}, 0.13 p_{C13}, 0.10 p_{C15}; L+1 = 0.31 p_{C4}, 0.16 p_{N1}, 0.14 p_{C8}, 0.11 p_{C6}. **3c**, H = 0.15 p_{O2}, 0.12 p_{C14}, 0.11 p_{C16}, 0.07 d_{Ni}; L = 0.29 p_{C17}, 0.14 p_{N2}, 0.14 p_{C13}, 0.10 p_{C15}; L+1 = 0.31 p_{C4}, 0.16 p_{N1}, 0.15 p_{C8}, 0.11 p_{C6}. **3d**, H = 0.10 p_{O1}, 0.10 p_{O2}, 0.09 d_{Ni}; L = 0.29 p_{C17}, 0.15 p_{N2}, 0.12 p_{C13}, 0.11 p_{C15}; L+1 = 0.30 p_{C4}, 0.16 p_{N1}, 0.15 p_{C8}, 0.11 p_{C6}. **3e**, H = 0.11 p_{O1}, 0.11 p_{O2}, 0.10 d_{Ni}; L = 0.24 p_{C17}, 0.11 p_{N2}, 0.09 p_{C13}, 0.08 p_{C15}; L+1 = 0.24 p_{C4}, 0.13 p_{N1}, 0.12 p_{C8}, 0.09 p_{C6}. **3f**, H = 0.14 p_{O2}, 0.12 p_{C14}, 0.09 p_{C16}, 0.09 d_{Ni}; L = 0.18 p_{C17}, 0.11 p_{C4}, 0.09 p_{N2}; L+1 = 0.18 p_{C4}, 0.12 p_{C17}, 0.10 p_{N1}, 0.10 p_{C8}, 0.07 p_{C6}. **3g**, H = 0.15 p_{O2}, 0.12 p_{C14}, 0.11 p_{C16}, 0.07 p_{O3}, 0.07 d_{Ni}; L = 0.24 p_{C17}, 0.12 p_{N2}, 0.11 p_{C13}, 0.08 p_{C15}; L+1 = 0.25 p_{C4}, 0.14 p_{N1}, 0.13 p_{C8}, 0.10 p_{C6}. **3h**, H = 0.11 d_{Ni}, 0.11 p_{O2}, 0.11 p_{O1}, 0.09 p_{C7}, 0.09 p_{C14}; L = 0.27 p_{C17}, 0.16 p_{C15}, 0.15 p_{N2}; L+1 = 0.24 p_{C4}, 0.20 p_{C6}, 0.14 p_{N1}. **3i**, H = 0.17 p_{O2}, 0.15 p_{C14}, 0.11 p_{C16}, 0.10 p_{Br}, 0.10 p_{C12}, 0.07 d_{Ni}; L = 0.19 p_{C17}, 0.10 p_{N2}, 0.08 p_{C6}, 0.08 p_{C13}, 0.07 p_{C15}; L+1 = 0.15 p_{C6}, 0.15 p_{C4}, 0.10 p_{C17}, 0.09 p_{N1}. **3j**, H = 0.18 p_{O2}, 0.17 p_{C14}, 0.11 p_{C16}, 0.11 p_{C12}, 0.09 d_{Ni}; L = 0.21 p_{C6}, 0.18 p_{C4}, 0.12 p_{N1}, 0.10 p_{N3}, 0.10 p_{O3}, 0.08 p_{O4}; L+1 = 0.27 p_{C17}, 0.13 $p_{N12,}$ 0.11 p_{C13}, 0.09 $p_{C15,}$, 0.09 d_{Ni}. **3k**, H = 0.18 p_{O2}, 0.17 p_{C14}, 0.12 p_{C16}, 0.10 p_{C12}, 0.08 d_{Ni}; L = 0.22 p_{C6}, 0.18 p_{C4}, 0.12 p_{N1}, 0.10 p_{N3}, 0.10 p_{O3}, 0.09 p_{O4}; L+1 = 0.27 p_{C17}, 0.13 p_{N2}, 0.12 p_{C13}, 0.10 p_{C15}, 0.09 d_{Ni}. **3k**, H = 0.16 p_{O2}, 0.14 p_{C14}, 0.12 p_{C16}, 0.09 $p_{O3(Me)}$,0.09 p_{C15}, 0.08 p_{C12}, 0.07 p_{N2}, 0.06 p_{C11}, 0.05 d_{Ni}; L = 0.22 p_{C6}, 0.18 p_{C4}, 0.12 p_{N1}, 0.10 p_{N3}, 0.10 $p_{O4(NO2)}$, 0.09 $p_{O5(NO2)}$; L+1 = 0.26 p_{C17}, 0.13 p_{N2}, 0.13 p_{C13}, 0.09 p_{C15}, 0.08 p_{C11}, 0.07 d_{Ni}. **Cu3a**, H = 0.13 p_{O1}, 0.12 p_{C7}, 0.11 p_{O2}, 0.10 p_{C14}, 0.09 p_{C5}, 0.08 p_{C9}, 0.07 p_{C16}, 0.06 p_{C12}; L = 0.61 d_{Cu}, 0.07 p_{O1}, 0.07 p_{O2}. **Cu3l**, H = 0.16 p_{O2}, 0.16 p_{C14}, 0.12 p_{C16}, 0.10 $p_{O3(Me)}$, 0.10 p_{C15}, 0.08 p_{C12}, 0.08 p_{C11}, 0.07 p_{N2}; L = 0.59 d_{Cu}, 0.08 p_{O2}, 0.06 p_{O1}. [c]Singularly occupied orbitals.

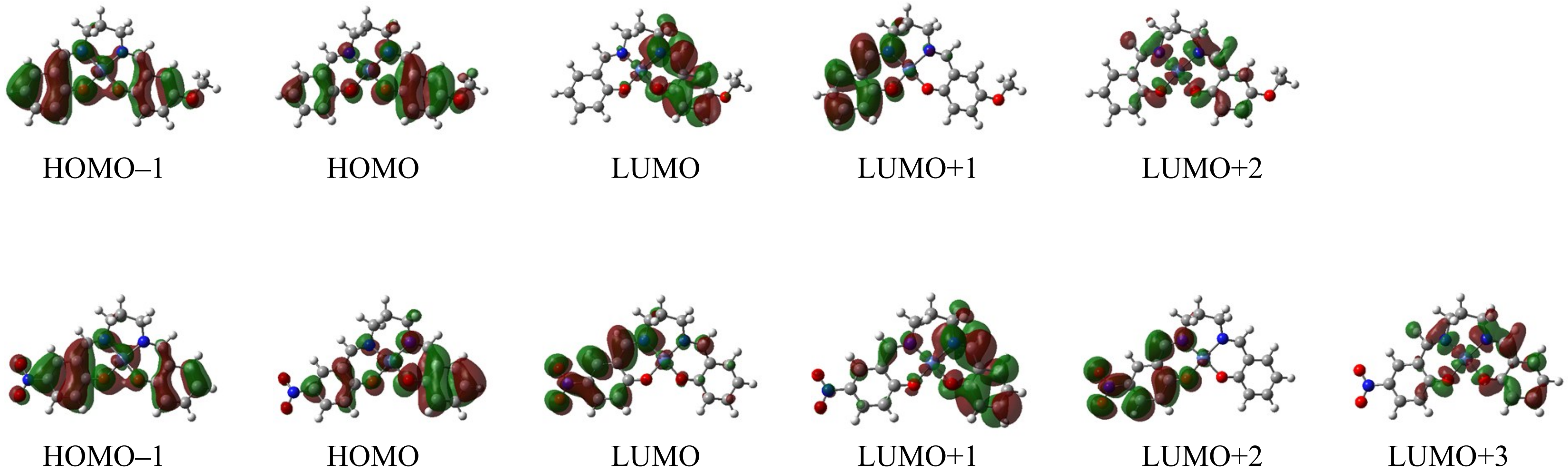

Fig. S1 Isodensity surface plot of the PBE0/6-311++G(d,p) frontier orbitals of **3c** (top) and **3j** (bottom) mainly involved in the computed transitions (isosurface values: 0.02).

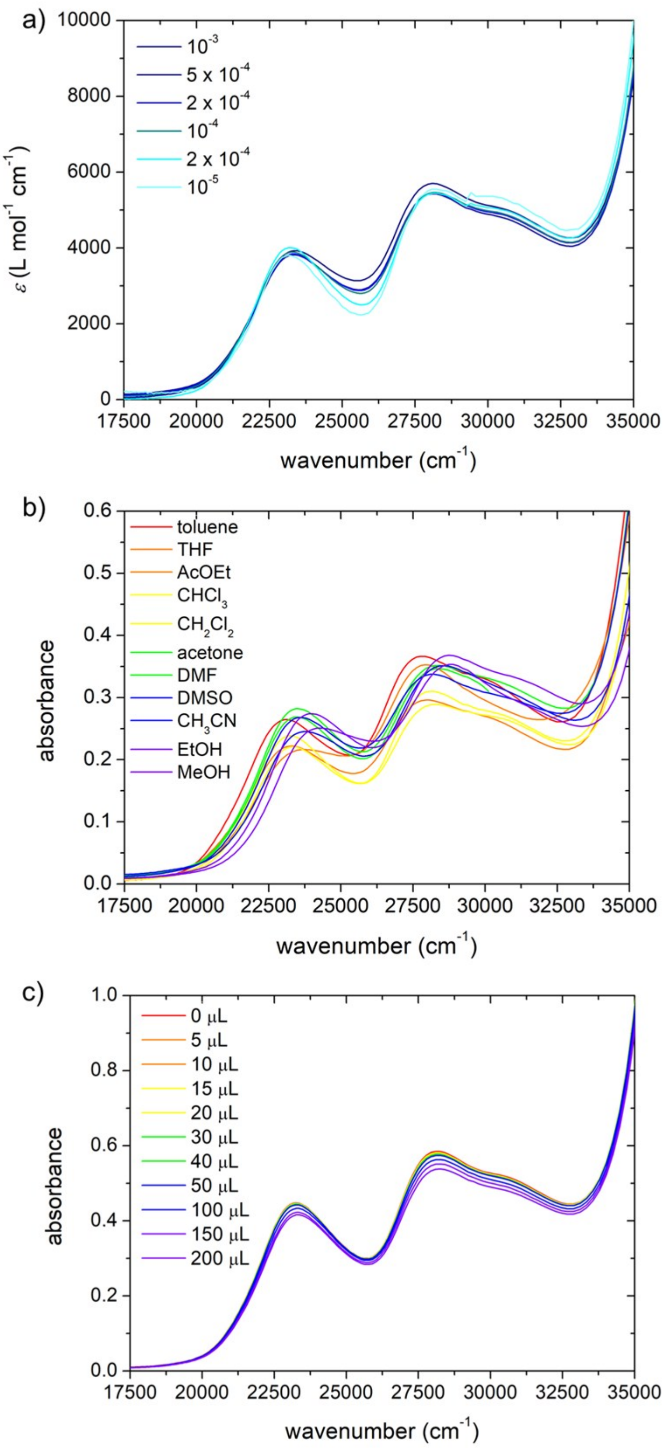

Fig. S2 UV-visible absorption spectra of **3c**: a) dilution studies from 10^{-3} down to 10^{-5} mol L^{-1} $CHCl_3$ solutions, b) solvatochromism at 5×10^{-5} mol L^{-1} solutions in solvents from low polar toluene (red) to high polar methanol (violet), and c) addition of increasing amount of DMSO (μL) to the 10^{-4} mol L^{-1} $CHCl_3$ solution (2 mL) (data were not corrected for the dilution given by the addition of DMSO).

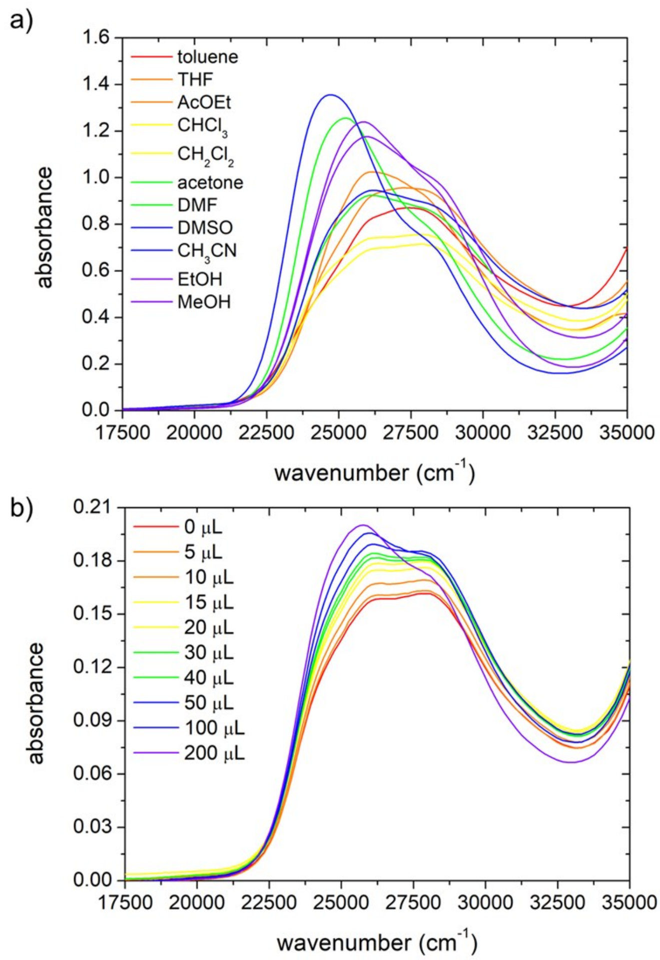

Fig. S3 UV-visible absorption spectra of **3j**: a) solvatochromism at 5×10^{-5} mol L^{-1} solutions in solvents from low polar toluene (red) to high polar methanol (violet), and b) addition of increasing amount of DMSO (μL) to the 10^{-4} mol L^{-1} $CHCl_3$ solution (2 mL) (optical path of 0.1 cm, data were not corrected for the dilution given by the addition of DMSO).

References

1 G. C. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2719–2726.

2 J. B. Hodgson and G. C. Percy, *Spectrochim. Acta A: Mol. Spectr.*, 1978, **34**, 777–780.

3 G. N. Tyson and S. C. Adams, *J. Am. Chem. Soc.*, 1940, **62**, 1228–1229.

4 R. H. Holm, *J. Am. Chem. Soc.*, 1961, **83**, 4683–4690.

5 J. Chakraborty, M. Nandi, H. Mayer-Figge, W. S. Sheldrick, L. Sorace, A. Bhaumik and P. Banerjee, *Eur. J. Inorg. Chem.*, 2007, **2007**, 5033–5044.

6 R. C. Elder, *Aus. J. Chem.*, 1978, **31**, 35–45.

7 A. Elmali, C. T. Zeyrek, Y. Elerman and I. Svoboda, *Acta Crystallogr. C*, 2000, **56**, 1302–1304.

8 O. Atakol, S. Durmus, Z. Durmus, C. Arici and B. Çiçek, *Synth. React. Inorg. Met.-Org. Chem.*, 2001, **31**, 1689–1704.