# The effect of *N*-methylation on the chemical reactivity of binuclear Ni amine-thiophenolate complexes†

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## Supporting information

*Characterization data:*

**2**: $^{1}H$ NMR (200 MHz, $CDCl_3$) $\delta$ 1.24 [s, 18 H, $C(CH_3)_3$], 2.34 (s, 6 H, N*H*), 2.81–2.91 [m, 16 H, $HN(CH_2CH_2)_2$], 3.15 [s, 4 H, $(ArSCH_2)_2$], 3.87 (s, 8 H, $ArCH_2NH$), 7.21 (s, 4 H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$) $\delta$ 32.2, 35.5, 38.1, 49.9, 50.4, 55.0, 128.4, 131.0, 145.1, 153.1.

**3**: mp 158 °C; $^{1}H$ NMR (200 MHz, $CDCl_3$) $\delta$ 1.21 [s, 18 H, $C(CH_3)_3$], 1.95 (s, 12 H, $ArCH_2NCH_3$), 2.19 [s, 6 H, $CH_3N(CH_2CH_2)_2$], 2.48–2.54 [m, 16 H, $CH_3N(CH_2CH_2)_2$], 3.02 [s, 4 H, $(ArSCH_2)_2$], 3.70 (s, 8 H, $ArCH_2NH$), 7.22 (s, 4 H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$) $\delta$ 31.7, 34.8, 37.8, 42.7, 43.2, 56.2, 56.6, 62.4, 126.7, 131.4, 144.5, 150.8.

**$H_2L^H$**: $^{1}H$ NMR (200 MHz, $D_2O$/DCl) $\delta$ 1.13 [s, 18 H, $C(CH_3)_3$], 3.33–3.45 [m, 16 H, $HN(CH_2CH_2)_2$], 4.46 (s, 8 H, $ArCH_2NH$), 7.52 (s, 4 H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (50 MHz, $D_2O$/DCl) $\delta$ 30.6, 34.5, 42.4, 44.3, 51.5, 131.3, 133.7, 152.4, one carbon signal was not observed.

**$H_2L^{Me}$**: $^{1}H$ NMR (200 MHz, $D_2O$/DCl): $\delta$ 1.29 [s, 18 H, $ArC(CH_3)_3$], 2.82 [s, 6 H, $CH_3N(CH_2CH_2)_2$], 2.86 (s, 12 H, $ArCH_2NCH_3$), 3.68–3.80 [m, 16 H, $CH_3N(CH_2CH_2)_2$], 4.53 (8 H, s, $ArCH_2NCH_3$), 7.48 (4 H, s, Ar*H*); $^{13}C\{^{1}H\}$ NMR (50 MHz, $D_2O$/DCl): $\delta$ 30.7, 34.1, 40.6, 40.8, 50.3, 51.8, 62.2, 131.2, 143.7, 147.7, one carbon signal was not observed.

**4**·$ClO_4$: IR (KBr, $cm^{-1}$): 3333, 3286, 3258, 3245 (NH), 1120, 1107, 1091 ($ClO_4^-$); UV-vis ($CH_3CN$): $\lambda_{max}$ 625 (58), 894 (54), 941 nm (56 $M^{-1}cm^{-1}$); CV ($CH_3CN$, 295 K, 0.1 M $^nBu_4NPF_6$, $E$ (V) vs SCE) $E^1_{1/2}$ = +0.27 ($\Delta E_p$ 91 mV); $E^2_{1/2}$ = +1.05 (irrev.). Anal. Calc. for $C_{32}H_{52}Cl_2N_6Ni_2O_4S_2$: C, 45.91; H, 6.26; N, 10.04; S, 7.66. Found: C, 44.42; H, 6.53; N, 9.67; S, 7.82. The perchlorate salt was additionally characterized by X-ray crystal structure analysis:

Refinement details: All non-hydrogen atoms were refined anisotropically except for the methyl carbon atoms of one rotationally disordered *t*Bu group. A split atom model was applied. The site occupancies of the respective orientations were refined as 0.62(2) (for C30a, C31a, C32a) and 0.38(2) (for C30b, C31b, C32b). Hydrogen atoms were assigned to idealized position and given a thermal parameter 1.2 times (1.5 for $CH_3$ groups) that of the atoms to which they are attached.

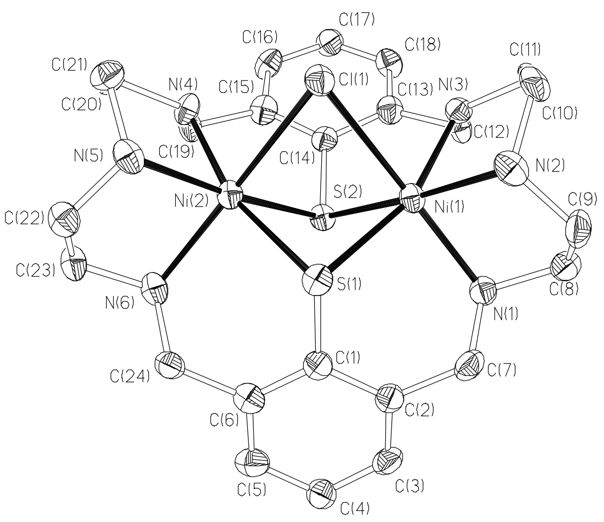


**Fig. S1** Structure of the $\mu$-Cl complex **4** with thermal ellipsoids drawn at the 50% probability level. *Tert*-butyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–Cl(1) 2.639(2), Ni(1)–S(1) 2.418(2), Ni(1)–S(2) 2.419(2), Ni(1)–N(1) 2.078(6), Ni(1)–N(2) 2.103(7), Ni(1)–N(3) 2.085(6), Ni(2)–Cl(1) 2.602(2), Ni(2)–S(1) 2.423(2), Ni(2)–S(2) 2.405(2), Ni(2)–N(4) 2.099(7), Ni(2)–N(5) 2.141(7), Ni(2)–N(6) 2.134(7); Ni···Ni 3.098(2).

**5**·$ClO_4$: IR (KBr, $cm^{-1}$): 1120, 1095 ($ClO_4^-$); UV-vis ($CH_3CN$): $\lambda_{max}$ 658 (41), 920 (59), 1002 nm (80 $M^{-1}cm^{-1}$); CV ($CH_3CN$, 295 K, 0.1 M $^nBu_4NPF_6$, $E$ (V) vs SCE) $E^1_{1/2}$ = +0.38 ($\Delta E_p$ 85 mV); $E^2_{1/2}$ = +1.37 (irrev.). Anal. Calc. for $C_{38}H_{64}Cl_2N_6Ni_2O_4S_2$: C, 49.54; H, 7.00; N, 9.12; S, 6.96. Found: C, 48.20; H, 6.73; N, 8.80; S, 6.64. The tetraphenylborate salt of **5** was characterized by X-ray crystal structure analysis:

Refinement details: There are two crystallographically independent molecules in the unit cell (PLATON was used to search for higher symmetry). All non-hydrogen atoms were refined anisotropically except for the methyl carbon atoms of one rotationally disordered *t*Bu group and the two molecules of methanol of crystallization. A split atom model was applied for the disordered *t*Bu group. The site occupancies of the respective orientations were refined as 0.52(2) (for C74a, C75a, C76a) and 0.48(2) (for C74b, C75b, C76b). Hydrogen atoms were assigned to idealized position and given a thermal parameter 1.2 times (1.5 times for $CH_3$ groups) that of the atoms to which they are attached.

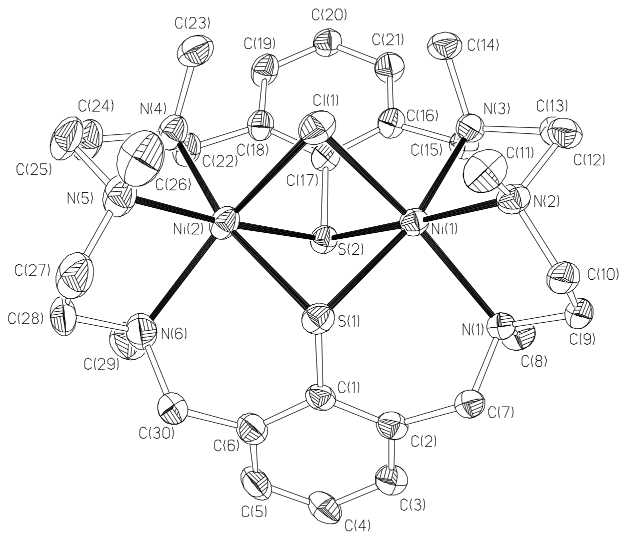


**Fig. S2** Structure of the $\mu$-Cl complex **5** with thermal ellipsoids drawn at the 50% probability level. *Tert*-butyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–Cl(1) 2.433(2) [2.516(2)], Ni(1)–S(1) 2.471(2) [2.475(2)], Ni(1)–S(2) 2.405(2) [2.407(2)], Ni(1)–N(1) 2.352(5) [2.349(5)], Ni(1)–N(2) 2.173(5) [2.173(5)], Ni(1)–N(3) 2.181(5) [2.167(5)], Ni(2)–Cl(1) 2.450(2) [2.455(2)], Ni(2)–S(1) 2.498(2) [2.483(2)], Ni(2)–S(2) 2.423(2) [2.371(2)], Ni(2)–N(4) 2.171(5) [2.222(7)], Ni(2)–N(5) 2.175(6) [2.172(5)], Ni(2)–N(6) 2.380(6) [2.375(5)]; Ni···Ni 3.184(2) [3.217(2)]. Values in square brackets represent the corresponding bond lengths for the other molecule.

**6**·$BPh_4$: IR (KBr, $cm^{-1}$): 3543 (OH), 733, 705 ($BPh_4^-$); UV-vis ($CH_3CN$): $\lambda_{max}$ 655 (48), 916 (36), 1047 nm (60 $M^{-1}cm^{-1}$); CV ($CH_3CN$, 295 K, 0.1 M $^nBu_4NPF_6$, $E$ (V) vs SCE) $E^1_{1/2}$ = +0.26 ($\Delta E_p$ 94 mV). Anal. Calc. for $C_{62}H_{85}BN_6Ni_2OS_2$: C, 66.33; H, 7.63; N, 7.49; S, 5.71. Found: C, 65.92; H, 7.23; N, 7.18; S, 5.47. The tetraphenylborate salt was additionally characterized by X-ray crystal structure analysis.

Refinement details: All non-hydrogen atoms were refined anisotropically except for the O atoms of the bridging hydroxide and the disordered methanol solvent molcule of crystallization. Anisotropic refinement of the O atom lead to large thermal ellipsoids. However, a split atom model could not be applied. The site occupancies of the two positions for the disordered methanol moleule were fixed to 0.5. Hydrogen atoms were assigned to idealized position and given a thermal parameter 1.2 times (1.5 for $CH_3$ groups) that of the atoms to which they are attached. No hydrogen atoms were calculated for the OH and the MeOH units.

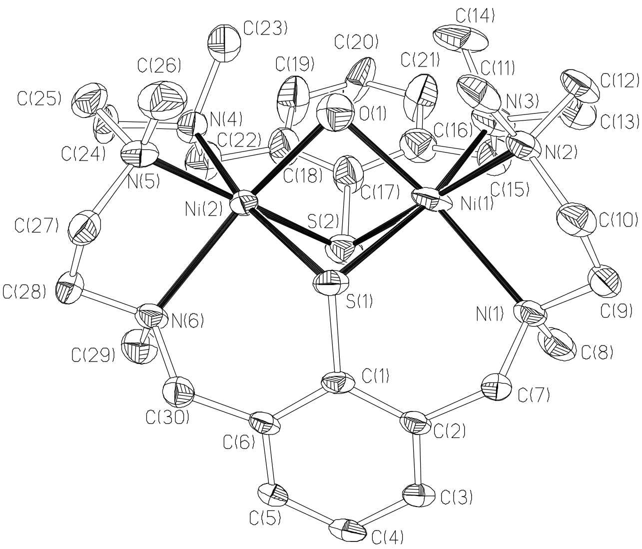


**Fig. S3** Structure of the $\mu$-OH complex **6** with thermal ellipsoids drawn at the 50% probability level. *Tert*-butyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)–O(1) 2.073(6), Ni(1)–S(1) 2.447(3), Ni(1)–S(2) 2.460(3), Ni(1)–N(1) 2.398(7), Ni(1)–N(2) 2.148(7), Ni(1)–N(3) 2.152(8), Ni(2)–O(1) 2.102(6), Ni(2)–S(1) 2.472(2), Ni(2)–S(2) 2.383(3), Ni(2)–N(4) 2.175(7), Ni(2)–N(5) 2.154(8), Ni(2)–N(6) 2.373(6); Ni···Ni 3.037(3).