

Electronic Supplementary Information

Complexation properties of the crown ether-containing *N*-thiophosphorylated thiourea towards Ni^{II}

Maria G. Babashkina,^a Damir A. Safin,^{*a} Koen Robeyns^a and Yann Garcia^a

^a *Institute of Condensed Matter and Nanosciences, MOST - Inorganic Chemistry, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. Fax: +32(0) 1047 2330; Tel: +32(0) 1047 2831; E-mail: damir.safin@ksu.ru*

Physical measurements: NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ¹H and ³¹P{¹H} NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and 85% H₃PO₄ (³¹P{¹H}). Electronic spectra of absorption in 10⁻⁴ M solution were measured on a Lambda-35 spectrometer in the range 200–1000 nm. Cyclic voltammetry was carried out at 100 mV/s scan rate in 0.1 M *n*Bu₄NPF₆ solutions using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a Gamry Series G 750 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal standard. Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

Synthesis of HL: A solution of 4'-aminobenzo-15-crown-5 (0.142 g, 0.5 mmol) in anhydrous CH₂Cl₂ (10 mL) was treated under vigorous stirring with a solution of (*i*PrO)₂P(S)NCS (0.131, 0.55 mmol) in the same solvent. The mixture was stirred for 1 h. The solvent was removed in a vacuum, and the colorless product was purified by recrystallisation from a 1:5 (v/v) mixture of CH₂Cl₂ and *n*-hexane. Yield: 0.238 g (91%). ¹H NMR δ (CDCl₃, ppm): 1.38 (d, ³J_{H,H} = 6.2 Hz, 12H, CH₃, *i*Pr), 3.75 (s, 8H, CH₂, crown ether), 3.90 (t, ³J_{H,H} = 4.4 Hz, 4H, CH₂, crown ether), 4.09–4.20 (m, 4H, CH₂, crown ether), 4.86 (d, s, ³J_{H,H} = 6.2 Hz, ³J_{POCH} = 10.6 Hz, 2H, OCH), 6.82–6.95 (m, 3H, C₆H₃), 7.00 (d, ³J_{PNH} = 7.9 Hz, 1H, PNH), 9.59 (s, 1H, arylNH). ³¹P{¹H} NMR δ (ppm): 52.9. *Anal.* Calc. for C₂₁H₃₅N₂O₇PS₂ (522.61): C 48.26, H 6.75, N 5.36. Found: C 48.31, H 6.70, N 5.39.

Synthesis of [Ni(L-1,5-S,S')₂]-2H₂O: A suspension of HL (0.157 g, 0.3 mmol) in aqueous EtOH (10 mL) was mixed with an aqueous EtOH (10 mL) solution of KOH (0.018 g, 0.33 mmol). An aqueous (10 mL) solution of NiCl₂ (0.023 g, 0.18 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with CH₂Cl₂, washed with water and dried with anhydrous MgSO₄. The solvent was then removed in vacuo. Dark green solid was isolated and washed with hot *n*-hexane (3 × 10 mL). Yield: 0.160 g (94%). ¹H NMR δ (CDCl₃, ppm): 1.10–1.82 (m, 24H, CH₃, *i*Pr), 3.75 (br. s, 16H, CH₂, crown ether), 3.89 (br. s, 8H, CH₂, crown ether), 4.12 (br. s, 8H, CH₂, crown ether), 4.65 (br. s, 2H, OCH), 4.93 (br. s, 2H, OCH), 5.30 (s, 2H, H₂O), 6.65–7.17 (m, 6H,

C₆H₃), 7.61 (br. s, 1H, arylNH), 10.91 (br. s, 1H, arylNH). ¹H NMR δ (acetone-*d*₆, ppm): 1.12 (d, ³J_{H,H} = 6.0 Hz, 12H, CH₃, *i*Pr), 1.18 (d, ³J_{H,H} = 6.0 Hz, 12H, CH₃, *i*Pr), 3.76 (s, 16H, CH₂, crown ether), 3.92 (s, 8H, CH₂, crown ether), 4.15 (br. s, 8H, CH₂, crown ether), 4.97 (br. s, 4H, OCH), 5.14 (s, 2H, H₂O), 6.71–7.09 (m, 6H, C₆H₃), 9.07 (br. s, 2H, arylNH). ³¹P{¹H} NMR δ (CDCl₃, ppm): 50.9 (2.8P), 53.5 (6P), 54.9 (1P), 58.2 (1P). ³¹P{¹H} NMR δ (acetone-*d*₆, ppm): 51.6. UV-Vis spectra (CH₂Cl₂), [λ_{max}, nm (ε, M⁻¹ cm⁻¹): 242 (21780), 318 (19787), 517 (211), 640 (199). UV-Vis spectra (acetone), [λ_{max}, nm (ε, M⁻¹ cm⁻¹): 251 (21105), 314 (2692), 545 (179), 678 (186). *Anal.* Calc. for C₄₂H₇₂N₄NiO₁₆P₂S₄ (1137.93): C 44.33, H 6.38, N 4.92. Found: C 44.26, H 6.31, N 4.87.

X-Ray crystallography: The X-ray data were collected on a STOE IPDS-II diffractometer with graphite-monochromatised Mo-K_α radiation generated by a fine-focus X-ray tube operated at 50 kV and 40 mA. The reflections of the images were indexed, integrated and scaled using the X-Area data reduction package.¹ Data were corrected for absorption using the PLATON program.² The structures were solved by direct methods using the SHELXS-97 program³ and refined first isotropically and then anisotropically using SHELXL-97.³ Hydrogen atoms were revealed from Δρ maps and those bonded to C were refined using appropriate riding models. H atoms bonded to N were freely refined. Figures were generated using the program Mercury.⁴

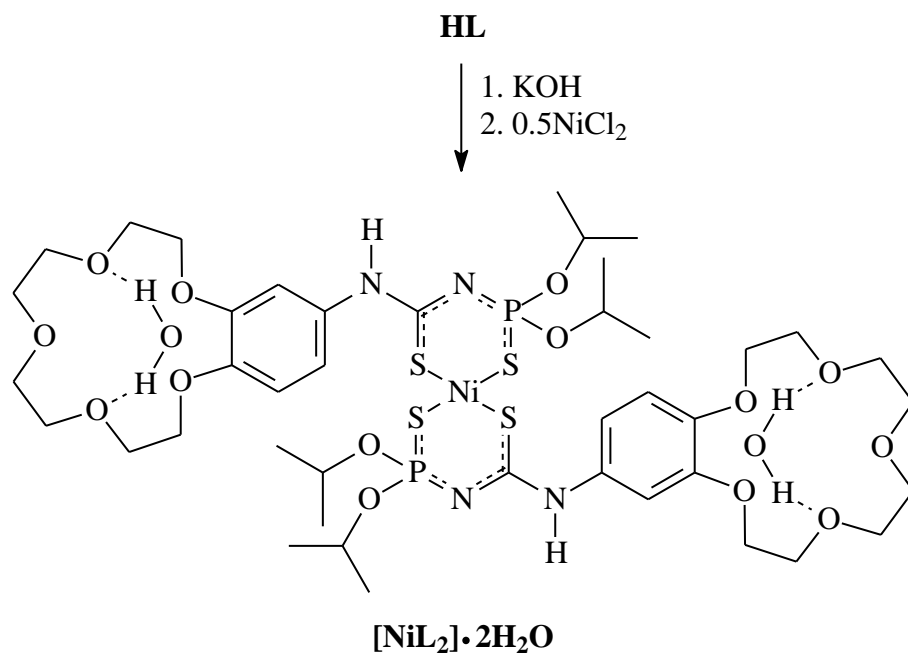
Crystal data for HL. C₂₁H₃₅N₂O₇PS₂, M_r = 522.60 g mol⁻¹, triclinic, space group *P* $\bar{1}$, *a* = 7.7391(3), *b* = 9.1558(11), *c* = 20.7496(17) Å, α = 83.459(8), β = 85.820(5), γ = 69.189(7)°, *V* = 1364.6(2) Å³, *Z* = 2, ρ = 1.272 g cm⁻³, μ(Mo-Kα) = 0.294 mm⁻¹, reflections: 4731 collected, 4731 unique, *R*_{int} = 0.048, *R*₁(all) = 0.0524, *wR*₂(all) = 0.1424.

Crystal data for [Ni(L-1,5-S,S')₂·2H₂O]. C₄₂H₇₂N₄NiO₁₆P₂S₄, M_r = 1137.93 g mol⁻¹, orthorhombic, space group *Pbca*, *a* = 23.4963(6), *b* = 8.2208(3), *c* = 29.2604(8) Å, *V* = 5651.9(3) Å³, *Z* = 4, ρ = 1.337 g cm⁻³, μ(Mo-Kα) = 0.612 mm⁻¹, reflections: 35470 collected, 5101 unique, *R*_{int} = 0.062, *R*₁(all) = 0.0444, *wR*₂(all) = 0.1080.

CCDC 848847 (**HL**) and 848848 ([**Ni(L-1,5-S,S')₂·2H₂O**]) contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- 1 Stoe & Cie. X-Area. Area-Detector Control and Integration Software. Stoe & Cie, Darmstadt, Germany, 2001.
- 2 A. L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148.
- 3 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
- 4 I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.*, 2002, **B58**, 389.



Scheme S1

Table S1. Selected electrochemical data for the nickel complex in CH₂Cl₂ (upper line) and acetone (bottom line)^a

E _{pa} (Ox 3)	E _{pa} (Ox 2)	E _{pa} (Ox 1)	E _{pa} (Red 1)	E _{pc} (Red 1)	E _{1/2} (Red 1)
—	1.15	0.72	-1.40	-1.53	-1.47
0.73	0.38	-0.06	-1.37	-1.48	-1.42

^aFrom cyclic voltammetry in 0.1 M *n*Bu₄NPF₆/solvent solutions at 100 mV/s scan rate. Potentials in V vs. FeCp₂⁺⁰. Half-wave potentials E_{1/2} for reversible processes, peak potential differences ΔE_{pp} = E_{pa} - E_{pc} in mV in parentheses (the value for ferrocene was 68 mV), cathodic peak potentials E_{pc} and anodic peak potentials E_{pa}.

Table S2. Selected bond lengths (Å) and angles (°) for **HL**

Bond lengths					
P(1)–N(3)	1.666(2)	S(5)–C(4)	1.654(3)	P(1)–O(7)	1.559(3)
N(3)–C(4)	1.389(3)	S(2)–P(1)	1.9214(13)	P(1)–O(11)	1.559(3)
N(6)–C(4)	1.350(3)				
Bond angles					
N(3)–C(4)–N(6)	111.3(2)	O(7)–P(1)–N(3)	109.03(13)	S(2)–P(1)–O(7)	114.61(10)
P(1)–N(3)–C(4)	130.6(2)	O(11)–P(1)–N(3)	103.69(12)	S(2)–P(1)–O(11)	117.10(12)
S(5)–C(4)–N(3)	123.37(19)	S(2)–P(1)–N(3)	109.29(10)	O(7)–P(1)–O(11)	102.31(16)
S(5)–C(4)–N(6)	125.29(19)				

Table S3. Selected bond lengths (Å) and angles (°) for [Ni(L-1,5-S,S')₂]**·2H₂O**

Bond lengths					
Ni(1)–S(2)	2.2178(7)	N(15)–C(5)	1.351(3)	P(3)–N(4)	1.586(2)
Ni(1)–S(6)	2.2114(6)	S(6)–C(5)	1.750(3)	P(3)–O(7)	1.556(3)
N(4)–C(5)	1.315(3)	S(2)–P(3)	1.9934(9)	P(3)–O(11)	1.573(2)
Bond angles					
Ni(1)–S(2)–P(3)	104.06(4)	N(4)–C(5)–N(15)	119.2(2)	S(2)–P(3)–N(4)	116.97(9)
Ni(1)–S(6)–C(5)	118.07(9)	O(7)–P(3)–N(4)	111.38(13)	S(2)–P(3)–O(7)	113.02(10)
S(2)–Ni(1)–S(6)	97.79(2)	O(11)–P(3)–N(4)	107.31(12)	S(2)–P(3)–O(11)	107.87(8)
S(2)–Ni(1)–S(2)a	180.00	O(7)–P(3)–O(11)	98.39(11)	S(6)–C(5)–N(4)	128.04(19)
S(2)–Ni(1)–S(6)a	82.21(2)	P(3)–N(4)–C(5)	128.77(18)	S(6)–C(5)–N(15)	112.68(19)

Table S4. Hydrogen Bond Lengths (Å) and Angles (°) for **HL** and **[Ni(L-1,5-*S,S'*)₂·2H₂O**

Compound	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
HL	N(3)–H(3)···O(30)	0.86	2.10	2.930(3)	163
	N(6)–H(6)···O(27)	0.86	2.33	3.064(3)	144
	N(6)–H(6)···O(30)	0.86	2.40	3.090(3)	137
[NiL₂]·2H₂O	N(15)–H(15)···O(51)	0.86	2.00	2.831(3)	162
	O(51)–H(51A)···O(31)	0.84	2.01	2.850(3)	178
	O(51)–H(51B)···O(25)	0.84	2.02	2.859(3)	173