



Dynamic behaviour of the complex $[\text{Ni}\{\text{PhC}(\text{S})\text{NP}(\text{O})(\text{OPr}^i)_2\text{-O}, \text{S}\}_2\text{-}\{\text{PhC}(\text{S})\text{NHP}(\text{O})(\text{OPr}^i)_2\text{-O}\}_2]$ in deuterotrchloromethane

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The title complex has been studied by ¹H and ³¹P NMR spectroscopy and found to undergo reversible dissociation of its neutral ligands and interconversion of its neutral and anionic ligands; the kinetic parameters of these processes and the crystal structure of the complex were determined; a new ligand exchange mechanism with unusual high spin–low spin transition during the ligand dissociation was suggested.

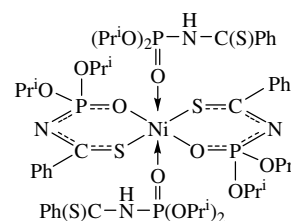
N-Thioacylamidothiophosphinates $\text{RC}(\text{S})\text{NHP}(\text{S})\text{R}'_2$ form square-planar NiL_2 complexes, where nickel is coordinated to four sulfur atoms.^{1,2} These complexes are capable of forming adducts with organic bases, for example, the mono and bis adducts of $[\text{PhC}(\text{S})\text{NP}(\text{S})(\text{OPr}^i)_2]_2\text{Ni}$ with pyridine (Py).³ Unlike these dithio ligands, *N*-diisopropoxyphosphorylthiobenzamide $\text{PhC}(\text{S})\text{-NHP}(\text{O})(\text{OPr}^i)_2$ (HL) forms a complex with Ni^{2+} having the formula $\text{NiL}_2(\text{HL})_2$.

The complex $\text{NiL}_2(\text{HL})_2$ was obtained by reacting a potassium salt of HL with $\text{Ni}(\text{NO}_3)_2$ in an aqueous ethanol solution.[†] Thiobenzamide is a weak acid and its potassium salt in water

also provides a source of neutral ligand HL, which coordinates to the complex NiL_2 to stabilise it. An excess of $\text{Ni}(\text{NO}_3)_2$ neutralises potassium hydroxide formed giving species such as $\text{Ni}(\text{OH})\text{NO}_3$ or $\text{Ni}(\text{OH})_2$.



The X-ray analysis of $\text{NiL}_2(\text{HL})_2$ shows the anionic ligands bind to nickel by oxygen and sulfur atoms, whilst the neutral ones do so by an oxygen atom.



[†] The NMR spectra were obtained on Varian Unity-300 and Bruker Avance 400 NMR spectrometers in CDCl_3 and $[\text{D}_8]\text{toluene}$ solutions, respectively. The ³¹P chemical shifts, in ppm, were recorded at 121.420 (Varian Unity-300) and 161.98 MHz (Bruker Avance 400). Chemical shifts were reported with reference to SiMe_4 (¹H) and H_3PO_4 (³¹P). ¹H NOESY experiment has been done at concentration of complex being 0.01 M. The electronic absorption spectra were measured on a Varian Cary 50 Bio spectrometer in the range 200–1100 nm. The IR spectra (Nujol) were recorded on a Specord M-80 spectrometer in the range 400–3600 cm^{-1} .

HL was obtained according to a previously reported procedure.¹⁶ $\text{NiL}_2(\text{HL})_2$ to the suspension of HL (1.13 g, 3.75 mmol) in ethanol (15 ml) a solution of KOH (0.21 g, 3.74 mmol) in 25 ml of the same solvent was added, and the mixture was stirred until HL dissolved completely. To the formed potassium salt under stirring a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.68 g, 2.34 mmol) in a mixture of water (30 ml) and ethanol (9 ml) was added dropwise. Precipitate formed. The resulting mixture was stirred for 2 h. Then, 25 ml of water and 15 ml of CH_2Cl_2 were added to the reaction mixture; the organic (lower) phase was separated, washed with water (five 50 ml portions) and dried over MgSO_4 . The solvents were removed in vacuum and the product was precipitated from benzene by *n*-hexane. Small lemon crystals formed. Yield 85% (relatively to the starting HL). Mp 136 °C. IR (ν/cm^{-1}): 3144 (b, NH), 1510 (s, S=C=N), 1328 (w, C=S), 1236 (m, P=O), 1150 (m, P=O), 1050–990 (vs., P–O–C). ¹H NMR (CDCl_3 , *c* 0.01 M, 298 K), neutral ligand signals $[\text{PhC}(\text{S})\text{NHP}(\text{O})(\text{OPr}^i)_2\text{-O}]$, δ : 1.23 (2br. d, 24H, Me), 4.52 (br. s, 4H, OCH), 7.53 (t, 4H, *m*-Ph, ³*J*_{HCH} 7.0 Hz), 7.60 (t, 2H, *p*-Ph, ³*J*_{HCH} 6.9 Hz), 8.14 (d, 4H, *o*-Ph, ³*J*_{HCH} 6.8 Hz), 8.94 (br. s, 2H, NH); anionic ligand signals $[\text{PhC}(\text{S})\text{NP}(\text{O})(\text{OPr}^i)_2\text{-S, O}]$: 1.54 (br. d, 12H, Me), 1.63 (br. d, 12H, Me), 4.96 (br. s, 4H, OCH), 7.23 (t, 2H, *p*-Ph, ³*J*_{HCH} 7.3 Hz), 7.66 (t, 4H, *m*-Ph, ³*J*_{HCH} 7.3 Hz), 7.79 (d, 4H, *o*-Ph, ³*J*_{HCH} 7.9 Hz). Found (%): C, 49.79; H, 6.45; N, 4.45. Calc. for $\text{C}_{52}\text{H}_{78}\text{N}_4\text{NiO}_{12}\text{P}_4\text{S}_4$ (1262.04) (%): C, 49.49; H, 6.23; N, 4.44.

The coordination polyhedron is an octahedron. The complex crystallises in space group $P2_1/n$, $Z = 2$, with nickel located at the centre of symmetry (Figure 1).[‡]

The Ni–S distance in $\text{NiL}_2(\text{HL})_2$ is 2.4091(4) Å, which is significantly longer than those found in the square-planar complex *cis*- $[\text{Et}_2\text{N}(\text{S})\text{NC}(\text{O})\text{Fc-O, S}]_2\text{Ni}$ (Fc = ferrocene): 2.147 and 2.149 Å.⁴ This can mainly be explained by its higher coordination number. The Ni–O(1A) distance [2.041(1) Å] is more comparable to the nickel–phosphoryl oxygen distance reported in the amido-phosphate complex with a NiO_6 core (2.083 Å).⁵ In $\text{NiL}_2(\text{HL})_2$, the anionic ligand bonds for C=S [1.724(2) Å] and P=O [1.492(1) Å] lengthen, while the P–N [1.620(2) Å] and C–N [1.303(2) Å] bonds shorten in comparison with those in free HL (C=S 1.646, P=O 1.457, P–N 1.672, C–N 1.360 Å) adopting intermediate values between those of single and double bonds.

The fragment S(1A)–C(1A)–N(1A)–P(1A)–O(1A) is almost planar, which is a characteristic of chelate complexes of XCNPO ligands.^{7–10} The SCNPO ring adopts a sofa conformation with the nickel atom deviating 0.9828 Å from the mean-square plane of the SCNPO fragment [planar within 0.031(2) Å]. In the neutral coordinating ligand the length of P=O bond is