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

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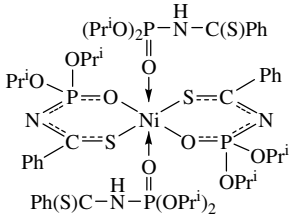
The title complex has been studied by ^{1}H and ^{31}P NMR spectroscopy and found to undergo reversible dissociation of its neutral ligands and interconversion of its neutral and anionic ligands; the kinetic parameters of these processes and the crystal structure of the complex were determined; a new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

N-Thioacylamidothiophosphinates RC(S)NHP(S)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 [PhC(S)NP(S)(OPr^i)$_2$]$_2$Ni with pyridine (Py).[3] Unlike these dithio ligands, *N*-diisopropoxyphosphorylthiobenzamide PhC(S)-NHP(O)(OPr^i)$_2$ (HL) forms a complex with Ni^{2+} having the formula $NiL_2(HL)_2$.

The complex $NiL_2(HL)_2$ was obtained by reacting a potassium salt of HL with $Ni(NO_3)_2$ 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 $Ni(NO_3)_2$ neutralises potassium hydroxide formed giving species such as $Ni(OH)NO_3$ or $Ni(OH)_2$.

$$KL + H_2O = HL + KOH$$
$$NiL_2 + 2HL = NiL_2(HL)_2 \quad (1)$$

The X-ray analysis of $NiL_2(HL)_2$ shows the anionic ligands bind to nickel by oxygen and sulfur atoms, whilst the neutral ones do so by an oxygen atom.



The 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 $NiL_2(HL)_2$ is 2.4091(4) Å, which is significantly longer than those found in the square-planar complex *cis*-[Et$_2$N(S)NC(O)Fc-*O*,*S*]$_2$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 an amido-phosphate complex with a NiO_6 core (2.083 Å).[5] In $NiL_2(HL)_2$, 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 SCNPONi 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

† The NMR spectra were obtained on Varian Unity-300 and Bruker Avance 400 NMR spectrometers in $CDCl_3$ and [$^2H_8$]toluene solutions, respectively. The ^{31}P 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 $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). ^{1}H 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]

NiL$_2$(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 $Ni(NO_3)_2 \cdot 6H_2O$ (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). ^{1}H NMR ($CDCl_3$, *c* 0.01 M, 298 K), neutral ligand signals [PhC(S)NHP(O)(OPr^i)$_2$-*O*], δ: 1.23 (2br. d, 24H, Me), 4.52 (br. s, 4H, OCH), 7.53 (t, 4H, *m*-Ph, $^3J_{HCCH}$ 7.0 Hz), 7.60 (t, 2H, *p*-Ph, $^3J_{HCCH}$ 6.9 Hz), 8.14 (d, 4H, *o*-Ph, $^3J_{HCCH}$ 6.8 Hz), 8.94 (br. s, 2H, NH); anionic ligand signals [PhC(S)NP(O)(OPr^i)$_2$-*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, $^3J_{HCCH}$ 7.3 Hz), 7.66 (t, 4H, *m*-Ph, $^3J_{HCCH}$ 7.3 Hz), 7.79 (d, 4H, *o*-Ph, $^3J_{HCCH}$ 7.9 Hz). Found (%): C, 49.79; H, 6.45; N, 4.45. Calc. for $C_{52}H_{78}N_4NiO_{12}P_4S_4$ (1262.04) (%): C, 49.49; H, 6.23; N, 4.44.

Table 1 The ligand HL exchange kinetic parameters and hyperfine coupling constants (A/h) in solutions containing $NiL_2(HL)_2$ and HL.

Solvent	$[NiL_2(HL)_2]$/mol dm^{-3}	[HL]/mol dm^{-3}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	k_{ex}/s^{-1} (298 K)	(A/h)/MHz
$[^2H_8]$toluene	0.0072	0.30	36.9±0.8	–15.9±1.3	2.85×10^5	7.1,[a] 6.1[b]
$CDCl_3$	0.0100	0.16	34.8±0.9	–24.6±3.8	2.55×10^5	3.4
	0.0071	0.30	35.3±1.0	–21.5±1.9	3.01×10^5	3.4[c]

[a]Value is from the $(T_{2p})^{-1}$–T dependence. [b]Value is from the $\Delta\omega_p$–T dependence. [c]The value was fixed at calculation.

1.468(1) Å, this being slightly longer than in the free ligand.[6] Similarly, the conformation of the OPN(H)C(S)C fragment is essentially unchanged upon coordination: the P=O and N–H groups are positioned *cis*, and the N–H and C=S groups are positioned *trans* relative to each other.

In solution the complex undergoes partial dissociation:

$$NiL_2(HL)_2 \rightleftarrows NiL_2(HL) + HL \rightleftarrows NiL_2 + 2HL \quad (2)$$

This equilibrium was studied by dynamic ^{1}H and ^{31}P NMR spectroscopy in deuterotrichloromethane and, for comparison, in $[^2H_8]$toluene.† Kinetic parameters for equilibrium (2) were obtained from the temperature dependence of the ^{31}P NMR spectra under a variety of HL concentrations in the temperature ranges 223–303 and 252–355 K for $CDCl_3$ and $[^2H_8]$toluene, respectively (see Figure 2).

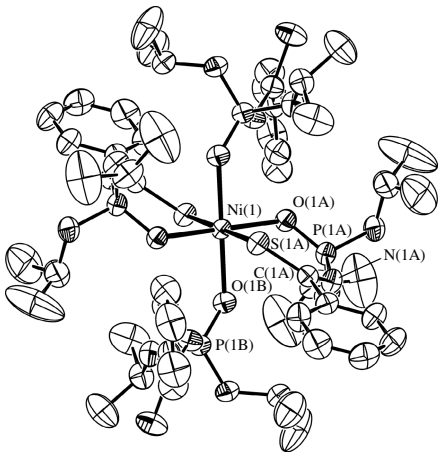


Figure 1 Crystal structure of the complex $NiL_2(HL)_2$, H atoms are not shown. Selected bond lengths (Å): Ni(1)–S(1A) 2.4091(4), Ni(1)–O(1A) 2.041(1), O(1A)–P(1A) 1.4921(12), S(1A)–C(1A) 1.7247(2), P(1A)–N(1A) 1.620(2), C(1A)–N(1A) 1.303(2), Ni(1)–O(1B) 2.135(1), O(1B)–P(1B) 1.4675(13); selected bond angles (°): S(1A)–Ni(1)–O(1A) 90.90(4), S(1A)–Ni(1)–O(1A′) (1 – x, –y + 1, –z) 89.10(4), Ni(1)–S(1A)–C(1A) 107.07(6), Ni(1)–O(1A)–P(1A) 123.05(7), P(1A)–N(1A)–C(1A) 129.37(13), O(1A)–P(1A)–N(1A) 120.16(7), S(1A)–C(1A)-N(1A) 128.9(1), Ni(1)–O(1B)–P(1B) 128.89(13).

‡ The X-ray diffraction data for the complex $NiL_2(HL)_2$ were collected at 20 °C on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoKα (λ = 0.71073 Å) radiation. Crystals of complex $C_{52}H_{78}N_4NiO_{12}P_4S_4$, monoclinic, a = 12.4796(7), b = 12.9525(7) and c = = 19.7409(10) Å, β = 95.369(1)°, V = 3177.0(3) Å^3, Z = 2, d_{calc} = 1.319 g cm^{-3}, space group $P2_1/n$ (molecule in special position). Cell parameters and intensities of 7432 independent reflections, from which 5817 with $I \geq 2\sigma$, were measured in the ω-scan mode, $\theta \leq 28.00°$. Absorption correction was not applied [μ(Mo) = 5.95 cm^{-1}]. The structure was solved by a direct method using the SIR[17] program and refined by the full matrix least-squares using the SHELXL97[18] program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms. All calculations were performed on PC using the WinGX[19] program. The final residuals were R_{ob} = 0.0348, R_{wob} = 0.0860. Data collections: images were indexed, integrated, and scaled using the APEX2 data reduction package.[20] Figures were made using the PLATON program.[21] The nickel(II) complex is isostructural to the cobalt(II) complex $CoL_2(HL)_2$ [space group $P2_1$/n, unit cell parameters are: a = 12.546(3), b = 12.930(2) and c = 19.695(7) Å, β = 95.45(4)°].[7]

CCDC 659836 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

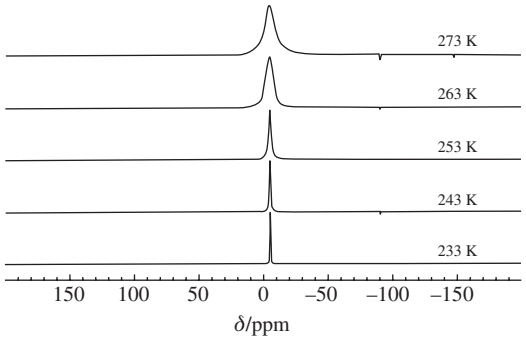


Figure 2 ^{31}P NMR spectra in $CDCl_3$ at different temperatures; concentrations of HL and $NiL_2(HL)_2$ are 0.30 M and 0.007 M, respectively.

Over the temperature range studied, the exchange between free HL in bulk solution (A) and that in the coordination sphere of $NiL_2(HL)_2$ (B) when [A] >> [B] satisfies the condition τ_B^{-2}, $\Delta\omega_B^2 >> T_{2B}^{-2}$. In this case, relations (3) and (4) apply:[11]

$$\frac{1}{T_{2p}} = \frac{1}{T_{2os}} + \frac{P_B}{\tau_B + (\tau_B\Delta\omega_B^2)^{-1}} \quad (3)$$

$$\Delta\omega_p = \Delta\omega_{os} + \frac{P_B}{\tau_B^2\Delta\omega_B + \Delta\omega_B^{-1}} \quad (4)$$

In equations (3) and (4), $(T_{2p})^{-1}$ and $\Delta\omega_p$ are the paramagnetic (p) contributions to the spin-spin relaxation rate and chemical shift, respectively, including minor outer-sphere (os) contributions, τ_B is the residence time of the bound HL ligand, $\Delta\omega_B$ is the chemical shift between the free and coordinated HL ligands, and P_M is the mole fraction of the bound HL ligand. The $\Delta\omega_B$ value is directly proportional to the hyperfine coupling constant (A/h) and inversely proportional to the temperature,[11] and the quantity τ_B related to the pseudo-first order exchange rate constant k_{ex} ($k_{ex} = \tau_B^{-1}$) depends on temperature according to the Eyring equation

$$\ln\frac{k_{ex}}{T} = \ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{R}\frac{1}{T}. \quad (5)$$

From the temperature dependence of $(T_{2p})^{-1}$ and $\Delta\omega_p$ in $[^2H_8]$toluene (Figure 3) and $(T_{2p})^{-1}$ in $CDCl_3$ (Figure 4) in accordance with

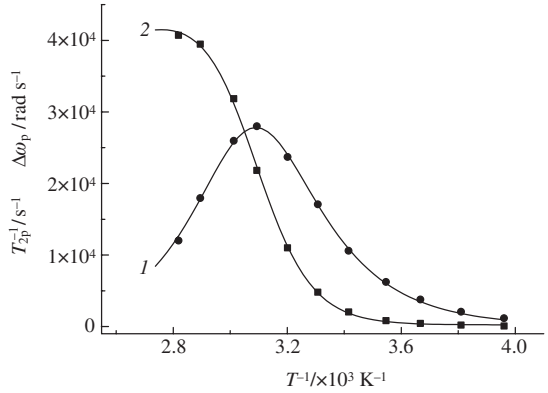


Figure 3 The experimental (points) and calculated (lines) temperature dependence of the parameters (*1*) $(T_{2p})^{-1}$ and (*2*) $\Delta\omega_p$ in the $[^2H_8]$toluene solution containing 0.30 M HL and 0.0072 M $NiL_2(HL)_2$.

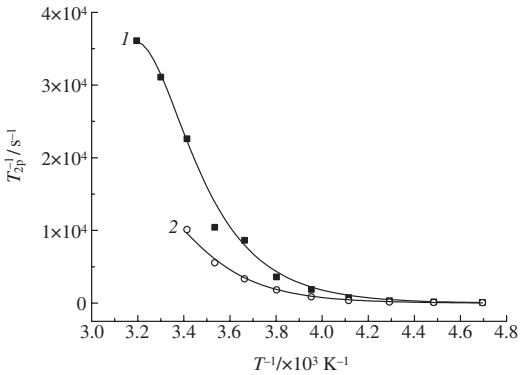


Figure 4 The experimental (points) and calculated (lines) temperature dependence of the $(T_{2p})^{-1}$ parameter in the $CDCl_3$ solutions containing (*1*) 0.16 M HL and 0.0100 M $NiL_2(HL)_2$ and (*2*) 0.30 M HL and 0.0071 M $NiL_2(HL)_2$.

relations (3)–(5), the kinetic parameters and coupling constants were calculated (Table 1).

The good fitting curves in Figures 3 and 4 suggest that the rate constant k_{ex} indeed relates to two-site exchange. In full agreement with this, the similar values of $\Delta H^{\neq}$, $\Delta S^{\neq}$ and k_{ex} found at different HL concentrations in the $CDCl_3$ solutions testify that the exchange reaction really is of first order and equilibrium (2) is almost completely shifted toward the $NiL_2(HL)_2$ form. The latter is supported by close correspondence of the electron absorption spectra parameters for $NiL_2(HL)_2$ [$\bar{\nu}_{max}$/cm^{-1} (ε_{max}/dm^3 mol^{-1} cm^{-1}): 17730 (65), 12860 (12) and 9190 (4) at 298 K in toluene with 0.0072 M $NiL_2(HL)_2$ and 0.10 M HL]† and for bis-adduct $[PhC(S)NP(S)(OPr^i)_2]_2NiPy_2$ but not for mono-adduct $[PhC(S)NP(S)(OPr^i)_2]_2NiPy$.[3]

In our opinion, the unexpected negative $\Delta S^{\neq}$ values found in two solvents can be explained by high spin–low spin transition at the formation of a five-coordinated intermediate $NiL_2(HL)$ in the dissociation of $NiL_2(HL)_2$. The smaller extension of an electronic shell (smaller ion radius) in the $NiL_2(HL)$ low-spin state results in decreasing the electron entropy and contracting the first coordination sphere with decreasing the molecule entropy. Such entropy reduction exceeds its increase at the dissociation of the HL ligand from $NiL_2(HL)_2$ and provides for the total negative activation entropy $\Delta S^{\neq}$. Previously,[12] the low-spin five-coordinated adducts of the complexes $[Ni(pyzs)]BF_4$ or $[Ni(pyrs)]BF_4$ (planar S_2N_2 coordination surroundings) with 1-methylimidazole in nitromethane solutions have been revealed. It is likely that the overall nucleophilicity and electronegativity of the donor atoms for these adducts and intermediate $NiL_2(HL)$ are similar and satisfy the Sacconi[13] correlation with the spin state. The reported[14] negative $\Delta S^{\neq}$ values in the exchange reactions for a series of solvent or base adducts with nickel(II) complexes may be accounted for in the same way. [An alternative explanation assumed that two HL ligands split out from $NiL_2(HL)_2$ simultaneously giving the low-spin NiL_2 intermediate appears as unlikely in view of too large positive contribution to $\Delta S^{\neq}$ from the dissociation of two ligands.] In this connection, it would be desirable to determine the activation volume ($\Delta V^{\neq}$) for such exchange reactions.

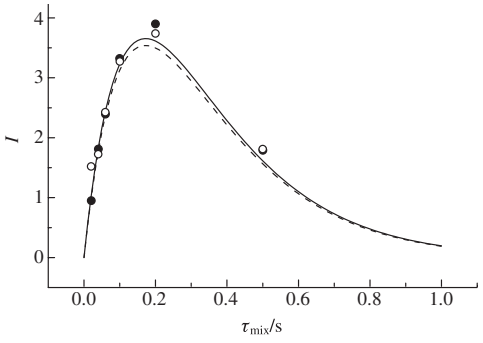


Figure 5 Integral intensities of Me protons exchange cross-peaks *versus* τ_{mix} in NOESY spectrum: experimental values for the first (open circles) and the second (solid circles) cross-peaks; theoretically calculated digenesis using full relaxation matrix analysis for first (dashed line) and second (solid line) ones.

The more negative $\Delta S^{\neq}$ values for $CDCl_3$ relative to $[^2H_8]$toluene indicate there is some assistance to the substitution of the leaving ligand from the deuterotrichloromethane molecule by means of H-bonding of the $CDCl_3$ with the coordinated phosphoryl oxygen of HL which is supported by decreasing the hyperfine coupling constant (A/h) in $CDCl_3$ (Table 1).

The NOESY spectra suggest that besides equilibrium (2) there is a slow intramolecular chemical exchange between neutral and anionic forms of coordinated ligand within the $NiL_2(HL)_2$ complex. Figure 5 shows the experimental and theoretical dependence of the Me proton exchange cross-peak integral intensities at different mixing times. The first-order rate constant, calculated for the exchange cross-peaks of the Me protons using full relaxation matrix analysis,[15] was found to be 0.89 s^{-1} (298 K).

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