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Synthesis and Single-crystal Characterization of the Square Planar Complex [Ni{$(SPPh_2)_2$N−S,S′}$_2$]·2THF

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Introduction

There have been numerous studies of the coordination chemistry of the tetra(alkyl,aryl)dithioimidodiphosphinate anion $[N(SPR_2)_2]^-$, which acts as a bidentate ligand that is able to form inorganic (carbon-free) chelate rings.[1−5] The interest in this type of ligand is due mainly to the high flexibility of the SPNPS system and the large S····S bite (ca. 4 Å). A variety of transition metal compounds have been characterized crystallographically, showing that the ligands form nonplanar metallocycles that may accommodate either tetrahedral or square planar coordination geometry.[6−9]

In particular, the bis(dithioimidophosphinato)nickel(II) chelates exhibit both tetrahedral and square planar coordination environments. Thus, the complexes obtained with the symmetric anionic ligands, [Ni{$(SPR_2)_2$N}$_2$] (R = Me, Ph),[10−12] present a tetrahedral NiS_4 core, while the complex prepared with the unsymmetrical ligand, [Ni{$(SPMe_2)(SPPh_2)$N}$_2$],[13] shows a square planar NiS_4 core. The existence of the tetrahedral environment is not yet understood because there are no steric factors present in the ligands which can destabilize a planar configuration with respect to a tetrahedral one. It is noteworthy that mononuclear sterically unencumbered chelates of nickel(II) with four coordinated sulfur atoms are generally diamagnetic with a square planar NiS_4 core.[13]

In this note, we report the preparation and crystallographic characterization of the square planar isomer [Ni{$(SPPh_2)_2$N−S,S′}$_2$]. Also, the square planar−tetrahedral isomerization process for this complex is briefly discussed.

Experimental Section

All operations were performed under purified nitrogen using Schlenk-tube techniques. THF was dried over Na−benzophenone ketyl and distilled under a nitrogen atmosphere. $Ni(CO)_4$ was purchased from a commercial source, and the ligand $HN(SPPh_2)_2$ was synthesized according to the literature procedures.[14] Elemental analysis (C, H, N, and S) was performed with a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. ^{1}H (200 MHz) and ^{31}P(81 MHz) NMR spectra were recorded on a Bruker AC-200P spectrometer, and the chemical shifts are reported in ppm relative to Me_4Si and 85% H_3PO_4 (positive shifts downfield) used as internal and external standards, respectively. The diamagnetic susceptibility was determined by the Gouy method. Electronic spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer.

2.1. Preparation of [Ni{$(SPPh_2)_2$N−S,S′}$_2$]·2THF. To a solution of the ligand $HN(SPPh_2)_2$ (1.0 g, 2.23 mmol) in 15 mL of tetrahydrofuran, $Ni(CO)_4$ (188 mg, 1.11 mmol) dissolved in 15 mL of tetrahydrofuran was added. The resulting solution was stirred at 40 °C for 1 h. During this time, the formation of powder nickel metal was observed. The mixture was filtered through diatomaceous earth, and the green solution obtained was concentrated under vacuum and cooled to −18 °C. Dark-green crystals were obtained after 7 days, which were separated by filtration, washed with pentane, and dried in a vacuum. Yield, 792 mg (65%). Anal Calcd. for $C_{56}H_{56}N_2NiO_2P_4S_4$: C, 61.0; H, 5.3; N, 2.5; S, 11.6. Found: C, 61.2; H, 5.1; N, 2.5; S, 11.7. Mp: 270−272 °C (dec). IR (KBr): $\nu_{as}(P_2N)$ 1150, 1112, and 832,; ν(PS) 565 cm^{-1}.

2.2. X-ray crystallography of [Ni{$(SPPh_2)_2$ N−S,S′}$_2$]·2THF: $C_{56}H_{56}N_2NiO_2P_4S_2$, M = 1099.86, green crystal of 0.56 × 0.40 × 0.22 mm size, triclinic, space group $P\bar{1}$, $a = 9.686(1)$, $b = 11.588(2)$, $c = 13.564(2)$ Å, $\alpha = 113.60(1)$, $\beta = 90.66(1)$, $\gamma = 99.98(2)°$, $V = 1368.5(3)$ Å^3, $Z = 1$, $\rho_c = 1.335$ Mg m^{-3}, μ(Mo Kα) = 0.667 mm^{-1}, $F(000) = 576$ (Table 1). Intensity data were collected on a Siemens $R3m$/v diffractometer in $\theta/2\theta$ scan method at 293(2) °K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). $1.64 < 2\theta < 27.56°$, $0 \le h \le 12$, $-15 \le k \le 14$, $-17 \le l \le 17$, 6698 reflections of which 6323 were independent ($R_{int} = 0.0142$) are used in all calculations. The structure was solved with direct methods and refined[15] by full-matrix least-squares on F^2 with anisotropic displacement parameters on all nonhydrogen atoms. H atoms were placed at geometrically idealized positions and refined using a riding model. Final $R(F) = 0.0451$ for 6323 reflections [$I > 2\sigma(I)$]; $wR(F^2) = 0.1310$ for all data, 313 parameters, goodness of fit = 1.058. Maximum peak and hole in final Fourier difference map +0.430 and −0.434 eÅ^{-3}, respectively.

Results and Discussion

The complex $Ni(CO)_4$ reacts with the ligand $HN(SPPh_2)_2$ in 1:2 molar ratio in tetrahydrofuran solution. Stable dark-green crystals were obtained by cooling the tetrahydrofuran solution at −18 °C. The isolated complex is diamagnetic in the solid

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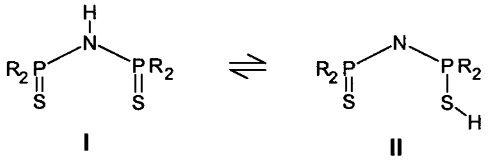
Table 1. Crystallographic Data and Structure Refinement for [Ni{(SPPh2)2N-S,S′}2]·2THF

chem. formula	$C_{56}H_{56}N_2NiO_2P_4S_4$	fw	1099.85
a	9.686(1) Å	space group	$P\bar{1}$
b	11.588(2) Å	*T*	20 °C
c	13.564 (2) Å	λ	0.71073 Å
α	113.60(1)°	ρ_{calcd}	1.335 Mg M^{-3}
β	90.66(1)°	μ (Mo Kα)	0.667 mm^{-1}
γ	99.98(2)°	R^a [*F*, $F<4\sigma(F)$]	0.0451
V	1368.5(3) Å^3	wR^b (F^2, all reflns)	0.1310
Z	1		

Scheme 1. Tautomeric (Thiol−Imido) Equilibrium



state, and its IR spectrum in KBr shows the absence of any carbonyl bands.

These results suggest the formation of a neutral nickel(II) complex, [Ni{$(SPPh_2)_2N$−S,S′}$_2$], which presents a square planar conformation in the solid state. It is interesting to note that the tetrahedral isomer of this compound was previously reported by Davison and Switkes, based on the reaction of [Et_4N][$NiCl_4$] with K[$(SPPh_2)_2N$], and the X-ray structure of the brown crystals revealed a tetrahedral NiS_4 core.[10] This latter isomer is paramagnetic in solution and in solid state. Oxidation from Ni(0) to Ni(II) under our conditions (inert atmosphere) might be explained as the result of the oxidative addition reaction of the imidodiphosphinate ligand to the Ni(0) center. Thus, IR and NMR spectroscopy of the free ligand support the existence of form **I** (Scheme 1) in the solid state,[16,21,22] whereas its reaction with diazomethane produces S-methyl ether derived from form **II**, revealing the existence of tautomeric equilibrium between imido−thiol forms in solution. On the other hand, oxidative additions of thiol forms to metal centers in low oxidation states are well known.[17] So, it is possible that the reaction through its tautomeric thiol form **II**, in solution, results in oxidation of the nickel atoms.

To obtain an unambiguous characterization of the isolated complex, an X-ray diffraction study was undertaken. Figure 1 shows a perspective ORTEP view of the complex, including the atom numbering scheme. In the molecular structure, the nickel atom displays a square planar coordination geometry, with two anionic [$(SPPh_2)_2N$]$^-$ ligands bonded through the sulfur atoms. The nickel atom occupies a center of inversion and is placed in the same plane as the sulfur atoms.

The complex exhibits a ladder type structure[13] with the NiS_2P_2N rings folded about the nonbonding P···S axis (Figure 2). The two planar fragments P(1)−N−P(2)−S(2) (maximum deviation from the mean plane is 0.114 Å for N) and P(1)−S(2)−Ni−S(1) (maximum deviation from the mean plane is 0.052 Å for P(1)) are inclined, with respect to each other, with a dihedral angle of 55.2 °.

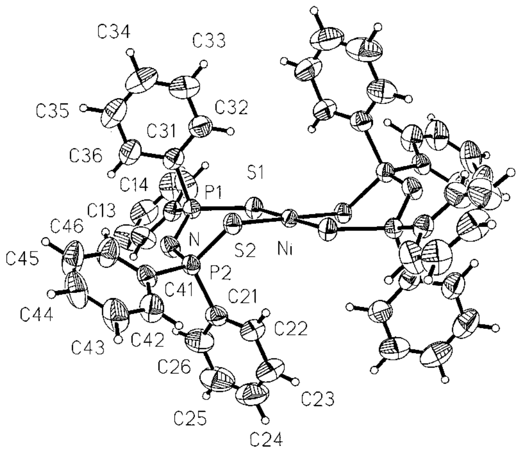


Figure 1. Molecular representation of the complex [Ni{$(SPPh_2)_2N$−S,S′}$_2$]·2THF. Selected bond distances (Å) and angles (deg): Ni−S(1) 2.2348(7); Ni−S(2) 2.2362(7); P(1)−N 1.600(2); P(2)−N 1.603(2); P(1)−S(1) 2.0321(9); P(2)−S(2) 2.0324(10); P(1)−C(11) 1.812(3); P(1)−C(31) 1.816(3); P(2)−C(21) 1.809(3); S(1)−Ni−S(2) 98.36; S(1)−Ni−S(1)$^\#$ 180.0; S(1)−Ni−S(2)$^\#$ 81.64(2); S(2)−Ni−(2)$^\#$ 180.0; P(1)−N−P(2) 119.82(13); Ni−S(1)−P(1) 112.52(3); Ni−S(2)−P(2) 106.15(4); N−P(1)−S(1) 118.19(9); N−P(2)−S(2) 115.67(9); N−P(1)−C(31) 110.80(12); N−P(1)−C(11) 106.10(12); N−P(2)−C(21) 110.15(13); N−P(2)−C(41) 107.94(11).

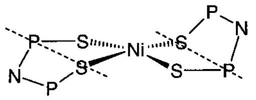


Figure 2. Ladder structure of the NiS_2P_2N rings.

Only a slight distortion of the NiS_4 core is observed. The endocyclic S−Ni−S angles (98.36 °) are longer than the exocyclic S−Ni−S angles (81.64 °). This behavior is similar to that observed in the square planar [Ni{$(SCMe)_2CH_2$}$_2$][18] and [Ni{$(SPMe_2)$ $(SPPh_2)$N}$_2$][13] complexes.

The Ni−S bond distances (2.2348(7) and 2.2362(7) Å) are slightly shorter than those found in the tetrahedral [Ni{$(SPPh_2)_2N$−S,S′}$_2$] isomer (Ni−S: average 2.299(12) Å) and are similar to those found in the square planar complex [Ni{$(SPMe_2)(SPPh_2)N$}$_2$] (Ni−S(Ph): average 2.231(1) Å).[13]

In the coordinated ligand, the P−S (2.0321(9) and 2.0324(10) Å) and P−N (1.600(2) and 1.603(2) Å) distances are intermediate between single and double bonds (P−S: average 2.097 Å; P═S: average 1.943 (free ligand); P−N: 1.780; P═N: 1.570 Å),[19] suggesting a partial electronic delocalization over the nonplanar SPNPS system. These distances compare well with those found in the similar square planar complex [Ni{$(SPMe_2)(SPPh_2)N$}$_2$] (P−S: average 2.032(1); P−N: average 1.600(2) Å)[4] and are longer than those found in the tetrahedral complex [Ni{$(SPPh_2)_2N$}$_2$] (P−S: average 2.018(2); P−N: average 1.559(5) Å).[10]

The square planar nickel complex is soluble in common organic solvents, such as THF, $CHCl_3$, CH_2Cl_2, C_6H_6, and acetone, to give pale-green solutions. The UV−vis spectra of these solutions exhibit only bands typical for the tetrahedral chromophore [Ni{$(SPPh_2)_2N$−S,S′}$_2$] between 700 and 800 nm.[10] The spectra show no temperature dependence in the range 0−25 °C. This might be explained if fast isomerization SP ⟹ Td occurs after dissolving the complex. The NMR spectra of the complex in deuterated solvents (THF-d_8, $CDCl_3$) show unexpected chemical shifts for a diamagnetic complex. Thus, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at very high field, δ − 459 ppm, and the ^1H NMR spectrum exhibits a highly resolved pattern of signals for the aromatic ring protons.

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These results suggest the existence of a paramagnetic complex in solution. This is due to a fast isomerization to a previously reported paramagnetic tetrahedral (T_d) isomer.[10]

Attempts to crystallize the previously described tetrahedral isomer complex[10] under our preparative conditions (low temperature, THF) always lead to formation of the square planar isomer. The same results are obtained in CH_2Cl_2 and $CHCl_3$ at low temperature. Slow evaporation of chloroform solutions at room temperature also produces only large green crystals corresponding to the SP isomer. Use of other solvents with higher dielectric constants, such as acetone, leads to the T_d isomer even at low temperature. In crystallizing the complex, both solvent polarity and temperature affect which will be isolated in the solid state. UV−vis spectra show that the isomeric equilibrium at room temperature is shifted mainly to the tetrahedral form in all solvents. Moreover, variable temperature $^{31}P\{^1H\}$ NMR experiments of the complex in THF-d_8 or CD_2Cl_2 solutions show that even at low temperature (−60 °C) the equilibrium SP $\Leftrightarrow$ T_d is displaced to the T_d form.

In the IR spectra, bands at 1150, 1112, and 832 cm^{-1} are assigned to νP_2N vibrational modes by analogies with other square planar complexes, $(Ni(SPMe_2)(SPPh_2)N$, $\nu_{as}(P_2N)$ 1150 vs)[13] and $(Ni\{(SePPh_2)_2N{-}Se,Se'\}_2$, $\nu_{as}(P_2N)$ 1166 m, 1108m, and 714 vs).[23]

Finally, Figure 3 shows the results of the IR experiments, in KBr pellets in the solid state, for the square planar and tetrahedral isomers. Thus, after heating a sample of the square planar isomer (**a**) at 130 °C for 30 min, the complex isomerizes to the tetrahedral form ($\nu(P_2N)$ 1205m, 1174m cm^{-1}),[20] and a mixture of both complexes is obtained (**b**). Alternatively, when the sample of the tetrahedral isomer (**c**) is cooled to −18 °C for 2 h, the complex isomerizes, and the same mixture (**b**) of both isomers ($\nu(P_2N)$ 1150 cm^{-1}) is obtained.

To the best of our knowledge, this is the first example of a tetrahedral $\Leftrightarrow$ square planar isomerism where both isomers have been structurally characterized.[10] It is also the first example, of which we are aware, of a reversible tetrahedral $\Leftrightarrow$ square planar isomerism in the solid state. Further investigations of this interesting system are underway.

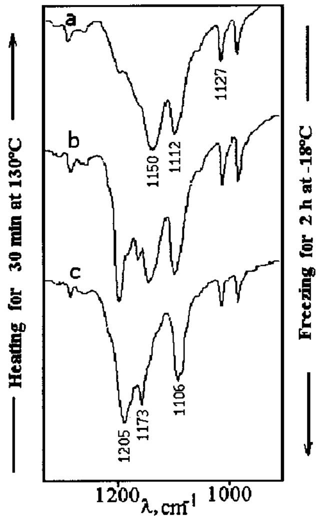

Figure 3. IR spectra in a KBr pellet of square planar (**a**), tetrahedral (**c**) isomers, and for a mixture of both isomers (**b**) as a result of isomerization process after heating square planar or freezing tetrahedral isomers.

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Supporting Information Available: X-ray crystallographic files, in CIF format for the structure determination of $[Ni\{(SPPh_2)_2N{-}S,S'\}_2]\cdot 2THF$. This material is available free of charge via Internet at http://pubs.acs.org.

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