Contribution from the Istituto di Chimica Generale e Inorganica,
Università, Laboratorio CNR, Florence, Italy

Sulfur Ligand–Transition-Metal Complexes. 3.[1,2] Mercapto Complexes of Nickel(II) with Tridentate Poly(tertiary phosphines). Crystal Structure of $[Ni(SH)(Ph_2PCH_2CH_2)_2NCH_2CH_2NH(C_2H_5)_2](BF_4)_2$

M. DI VAIRA, S. MIDOLLINI, and L. SACCONI*

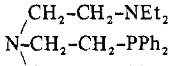
Received July 21, 1977

The poly(tertiary phosphine) ligands bis(2-diphenylphosphinoethyl)-*n*-propylamine (pnp), bis(2-diphenylphosphinoethyl)phenylphosphine (ppp), and *N*,*N*-bis(2-diphenylphosphinoethyl)-2′-diethylaminoethylamine (n_2p_2) form stable thiol complexes of nickel(II), acting as tridentate ligands. The ligand n_2p_2, which is potentially tetradentate, behaves as tridentate because one of its nitrogen atoms is quaternized by the uptake of a proton from the reactant HSR. The general formulas of the compounds are $[Ni(SR)(pnp)]BPh_4$, $[Ni(SR)(ppp)]BPh_4$, and $[Ni(SR)(n_2p_2H)]Y_2$ (R = H, CH_3; n_2p_2H = quaternized n_2p_2 ligand; Y = ClO_4, BF_4). The complexes are diamagnetic and square planar. The x-ray structure determination of $[Ni(SH)(n_2p_2H)](BF_4)_2$ (orthorhombic, *Pna*2_1, a = 23.987 (8) Å, b = 21.932 (8) Å, c = 7.163 (3) Å) has shown that the metal atom is coordinated by one nitrogen and two phosphorus atoms of the ligand n_2p_2H and by the sulfur atom (Ni–N 2.005 (8); Ni–P 2.190 (3), 2.188 (3); Ni–S 2.144 (3) Å) in a distorted square-planar arrangement.

Introduction

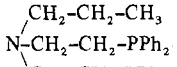
In recent years the sulfur ligand–transition-metal complexes have attracted considerable interest.[3-5] However, thiol complexes of transition metals are still rare. In previous papers we have reported that some tripod-like poly(tertiary phosphines), such as tris(2-diphenylphosphinoethyl)phosphine (pp_3) and tris(2-diphenylphosphinoethyl)amine (np_3), are capable of forming stable mercapto and methylthio complexes of 3d transition metals.[1,2] Low-spin complexes with the formula $[M(SR)L]BPh_4$ (R = H, CH_3; L = pp_3, M = Fe, Co, Ni; L = np_3, M = Co, Ni) and the complex $[Ni(SH)(np_3)]$ have been prepared and characterized. All of them possess essentially trigonal-bipyramidal coordination geometry.

The remarkable stability of these complexes has stimulated us to pursue the investigation, using more poly(tertiary phosphines) as coligands. In the course of this study we have found that the potentially tetradentate ligand *N*,*N*-bis(2-diphenylphosphinoethyl)-2′-diethylaminoethylamine (n_2p_2) forms



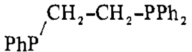
$$N\begin{cases}CH_2\text{-}CH_2\text{-}NEt_2\\CH_2\text{-}CH_2\text{-}PPh_2\\CH_2\text{-}CH_2\text{-}PPh_2\end{cases}$$

n_2p_2



$$N\begin{cases}CH_2\text{-}CH_2\text{-}CH_3\\CH_2\text{-}CH_2\text{-}PPh_2\\CH_2\text{-}CH_2\text{-}PPh_2\end{cases}$$

pnp



$$PhP\begin{cases}CH_2\text{-}CH_2\text{-}PPh_2\\CH_2\text{-}CH_2\text{-}PPh_2\end{cases}$$

ppp

nickel(II) complexes with the formula $[Ni(SR)(n_2p_2H)]Y_2$ (R = H, CH_3; n_2p_2H = quaternized n_2p_2 ligand; Y = BF_4, ClO_4) in which it acts as tridentate because one of its nitrogen atoms is quaternized by transfer of a proton from the HSR reactant to the ligand. The fact that the above n_2p_2 complexes are actually –SR rather than –SHR derivatives is supported by the comparison with nickel(II) complexes formed with the tridentate ligands bis(2-diphenylphosphinoethyl)-*n*-propylamine (pnp) and bis(2-diphenylphosphinoethyl)phenylphosphine (ppp), which turn out to be unequivocally –SR derivatives. The latter compounds have the formulas $[Ni(SR)(pnp)]BPh_4$ and $[Ni(SR)(ppp)]BPh_4$ (R = H, CH_3).

All of these complexes have been characterized by means of magnetic, spectrophotometric, and conductivity measurements.

The structure of the complex $[Ni(SH)(n_2p_2H)](BF_4)_2$ has been determined by x-ray diffraction methods.

Experimental Section

Reagents. All solvents were reagent grade. H_2S, CH_3SH, and $NaBPh_4$ were AR grade. Both the perchlorate and tetrafluoroborate of nickel(II) were prepared from the metal carbonate by addition of the corresponding acid and then recrystallized from aqueous solutions. The syntheses of the ligands n_2p_2 and pnp appear elsewhere.[6,7] The ligand ppp was acquired from the Pressure Chemical Co., Pittsburgh, Pa.

Preparation of the Complexes. All reactions were carried out in a dry nitrogen atmosphere and the complexes were dried by standing in a dry nitrogen current.

$[Ni(SH)(n_2p_2H)]Y_2$, Y = BF_4, ClO_4. One millimole of $[Ni(H_2O)_6]Y_2$ in 20 mL of C_2H_5OH was added at room temperature to a solution of 1 mmol of the ligand n_2p_2 in 20 mL of CH_2Cl_2. Hydrogen sulfide was bubbled into the resulting solution until a definite change of color took place (ca. 3 min). Concentration of the solution under nitrogen at room temperature led to the precipitation of crystals which were filtered off and washed with ethanol and petroleum ether.

$[Ni(SH)L](BPh_4)$, L = pnp, ppp. These complexes were prepared by a method analogous to that used for the above compounds, except that DMF was used in the place of CH_2Cl_2. Crystals of the tetraphenylborate salts were obtained by addition of $NaBPh_4$.

$[Ni(SCH_3)(n_2p_2H)](BF_4)_2$; $[Ni(SCH_3)L]BPh_4$, L = pnp, ppp. These compounds were prepared in the same way as the corresponding mercapto derivatives, but using CH_3SH in the place of H_2S.

Physical Measurements. The physical measurements were executed by the previously described methods.[8] See Table I for analytical and conductivity data.

Collection and Reduction of X-Ray Intensity Data. Crystals of the compound $[Ni(SH)(n_2p_2H)](BF_4)_2$, prepared as described above, were used for the crystallographic measurements and for data collection. A Philips PW 1100 automated diffractometer and monochromated Cu Kα radiation (λ 1.5418 Å) were used for all operations. Systematic absences ($h0l$), $h = 2n + 1$, ($0kl$), $k + l = 2n + 1$, ($h00$), ($0k0$), and ($00l$), h, k, and $l = 2n + 1$, establish the space group as the acentric *Pna*2_1 of the orthorhombic system. Cell constants, determined by least-squares refinement of the setting angles of 20 reflections, are a = 23.987 (8), b = 21.932 (8), and c = 7.163 (3) Å. The measured density value of 1.43 g cm^{-3} (by flotation in aqueous K_2HgI_4 solution) agrees with that of 1.422 g cm^{-3} calculated for four formula units of $C_{34}H_{44}B_2F_8N_2Ni_1P_2S_1$ in the cell. The crystal used for data collection was an elongated plate with dimensions of 0.03 × 0.15 × 0.90 mm along the [100], [010], and [001] directions, in that order. The intensity data were collected in the interval $4 \leq 2\theta \leq 135°$, at a 4.5° takeoff angle, by the ω–2θ scan technique, with a symmetric scan range of $1.20 + 0.10 \tan\theta$ (deg) and a scan speed of 3.0°/min in 2θ. Stationary background countings were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections, monitored every 100 min, showed an overall linear decrease of ca. 4% in intensities during data collection, due to slow decomposition of the material. Data sets were properly rescaled and processed using a 0.05 value for p.[9] A total of 2430 reflections having $I \geq 3\sigma(I)$ were considered observed and included in subsequent calculations. The value of the linear absorption coefficient, μ, is 26.47 cm^{-1} for Cu Kα radiation. Transmission factors ranged from 0.56 to 0.91, and a correction for absorption was applied. The principal computer programs used are listed in ref 1.

Solution and Refinement of the Structure. The structure of $[Ni(SH)(n_2p_2H)](BF_4)_2$ was solved by standard heavy-atom procedures. A series of Fourier syntheses yielded the positions of all atoms heavier than hydrogen. Full-matrix least-squares refinement min-

0020-1669/78/1317-0816$01.00/0

Table I. Analytical and Physical Data for the Complexes

Compd	Color	% C		% H		% N		% Ni		% S		Λ_M,[a] cm^2 Ω^{-1} mol^{-1}
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$[Ni(SH)(n_2p_2H)](BF_4)_2$	Brown	50.60	50.77	5.50	5.28	3.47	3.45	7.28	6.99	3.97	3.76	104
$[Ni(SH)(n_2p_2H)](ClO_4)_2$	Brown	49.06	49.10	5.33	5.44	3.37	3.44	7.05	6.85	3.85	3.78	89
$[Ni(SCH_3)(n_2p_2H)](ClO_4)_2$	Greenish	49.67	50.32	5.48	5.50	3.31	3.22	6.94	7.15	3.79	3.88	87
$[Ni(SH)(pnp)]BPh_4$	Red	73.84	74.70	6.31	6.62	1.57	1.52	6.56	6.70	3.58	3.39	58
$[Ni(SCH_3)(pnp)]BPh_4$	Green	74.03	74.23	6.43	6.66	1.54	1.50	6.82	6.56	3.53	3.30	51
$[Ni(SH)(ppp)]BPh_4$	Yellow	73.67	73.93	5.76	6.15			6.21	6.00	3.39	3.27	51
$[Ni(SCH_3)(ppp)]BPh_4$	Orange	73.85	74.28	5.88	6.23			6.12	6.11	3.34	3.21	50

[a] Molar conductance values for 10^{-3} M nitroethane solution.

imized the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. The z coordinate of the nickel atom was not allowed to change during the least-squares cycles, due to the polar nature of the space group. In the final cycles anisotropic thermal parameters were used for all atoms heavier than carbon in the complex cation and for the carbon atoms of the nonchelating chain of the n_2p_2H ligand. Atoms of the anions were also refined anisotropically. The total number of parameters refined was 311. Hydrogen atoms of the phenyl and methylene groups were introduced in calculated positions (C–H = 1.00 Å, positions being recalculated every few refinement cycles) as fixed contributions, each with a temperature factor ca. 15% larger than that of the carbon atom to which it was attached. Methyl hydrogen atom positions, located from difference-Fourier syntheses, were idealized to produce a tetrahedral arrangement about the carbon atom by a least-squares procedure. Atomic scattering factors were taken from ref 10, and anomalous dispersion terms for the nickel, sulfur, and phosphorus atoms were included in F_c.[11] A ΔF Fourier map calculated at $R = 0.075$ showed one peak with a height of 0.9 e Å^{-3} in the proximity of the metal atom and a few dispersed peaks with height ≤0.4 e Å^{-3}. Two peaks with heights of ca. 0.4 e Å^{-3} lay at distances of ca. 1.0 Å from the sulfur atom. They were close to the best plane through the metal and the four coordinating donor atoms and were symmetrically displaced from the plane orthogonal to the previous one, passing through the nitrogen and sulfur atom positions. The presence of such peaks was suggestive of a coordinating $-SH_2$ group or of an $-SH$ group with the hydrogen atom position affected by twofold disorder. Least-squares refinement in which these two "hydrogen atoms" were added to the model with unit population parameters, a 0.5 damping factor being applied on all shifts, slowly converged. At the end of this set of cycles the temperature factors of the two "hydrogen atoms" were high, and their positions were essentially consistent with those in the ΔF Fourier synthesis. As the improvement in R was not statistically significant[12] and as it was impossible to determine from the x-ray data alone the exact number of hydrogen atoms bonded to sulfur, such hydrogens were not included in the final refinement. However, the x-ray evidence for existence of (one or two) hydrogen atoms attached to the sulfur atom cannot be neglected. Refinement was halted at $R = 0.073$ and $R_w = 0.087$ when no shift was larger than 0.4 times the corresponding esd, calculated from the least-squares matrix, and the average value of the shift per error ratios was <0.05 (the error in observation of unit weight was 1.80; R_w is defined as $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$). The final positional and thermal parameters appear in Table II. A listing of the observed and calculated structure amplitudes is available.[13] The positional parameters reported in Table II probably pertain to the absolute configuration of the compound because a refinement in which the signs of the z coordinates of all atoms were reversed converged to an R value of 0.075, slightly higher than that above.

Results and Discussion

All compounds are air stable in the solid state but decompose slowly in polar organic solvents, even under an inert atmosphere. They are all diamagnetic.

The complexes formed by the n_2p_2 ligand behave as 1:2 electrolytes (Table I). They could be assigned two alternative formulas, namely, $[Ni(SHR)(n_2p_2)]Y_2$ or $[Ni(SR)(n_2p_2H)]Y_2$, where n_2p_2H denotes the n_2p_2 ligand in which one nitrogen atom has accepted a proton released by H_2S. In fact, complexes formed by quaternized ligands have already been described.[14] The IR spectrum of the above compounds, showing an intense band at ca. 3100 cm^{-1}, which may be unequivocally assigned to the N^+–H stretching vibration,[14] provides decisive support for the alternative formulation of the compound as an –SR derivative.

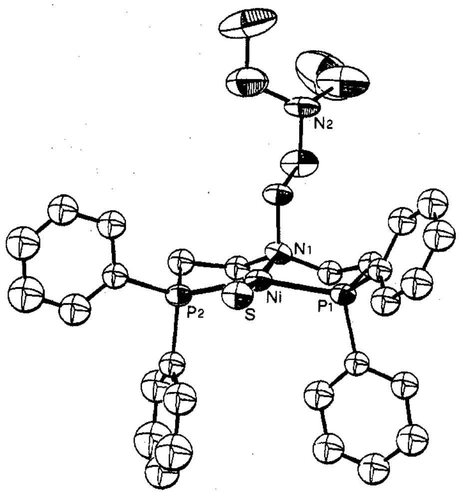


Figure 1. Perspective view of the cation in the structure of $[Ni(SH)(n_2p_2H)](BF_4)_2$.

The structure of the complex $[Ni(SH)(n_2p_2H)](BF_4)_2$ determined by x-ray analysis consists of $[Ni(SH)(n_2p_2H)]^{2+}$ cations and of BF_4^- anions, in the ratio of 1:2. The nickel atom is coordinated by the two phosphorus atoms, by the central nitrogen atom of the ligand, and by the sulfur atom, which form a distorted square-planar environment (Figure 1). Deviations from the planar arrangement of the donor atoms, probably caused by geometric requirements of the ligand and by steric repulsions, are essentially due to the fact that both the P1–Ni–P2 and N1–Ni–S angles are less than 180°; they measure 157.0 (1) and 170.1 (2)°, respectively. This produces an overall small distortion toward tetrahedral coordination. Distances and angles about the metal atom and selected values for the rest of the cation appear in Table III.[15]

The peripheral nitrogen atom of the n_2p_2 ligand does not coordinate to the metal, so it is identified as the nitrogen which is quaternized. Additional evidence for this is provided by the fact that *both* BF_4^- ions lie close to the nonchelating chain of the tripod ligand and form several short contacts with it. The shortest one is a N2···F1 nonbonded distance of 2.90 Å. Also, the positions of the BF_4 groups are not affected by disorder, at variance with what is commonly found in absence of electrostatic interactions.

The average of the B–F distances, uncorrected for thermal motion, is 1.31 (4) Å. The noncoordinating nitrogen atom lies at a distance of 5.23 Å from the metal and there are no close intermolecular approaches to the metal atom: the shortest one is a 4.48-Å Ni···F6 (x, y, z) contact. There are no short intermolecular contacts in the structure, with the exception of those mentioned above, formed by the BF_4 groups.

Table II. Atomic Parameters for $[Ni(SH)(n_2p_2H)](BF_4)_2$[a]

	x	y	z	U, Å^2		x	y	z	U, Å^2
Ni[b]	0.1836 (1)	0.1043 (1)	0.5029		C12	0.2401 (5)	−0.0684 (6)	0.721 (2)	0.052 (3)
S	0.1355 (1)	0.1053 (2)	0.7548 (4)		C13	0.2463 (5)	−0.1116 (6)	0.868 (2)	0.062 (4)
P1	0.1791 (1)	0.0049 (1)	0.4760 (4)		C14	0.2008 (6)	−0.1329 (6)	0.955 (2)	0.066 (4)
P2	0.1658 (1)	0.1996 (1)	0.4342 (4)		C15	0.1490 (6)	−0.1136 (6)	0.910 (2)	0.068 (4)
F1	0.3604 (4)	−0.0059 (5)	0.595 (2)		C16	0.1416 (5)	−0.0697 (6)	0.772 (2)	0.057 (3)
F2	0.4349 (6)	0.0219 (8)	0.755 (2)		C17	0.1151 (4)	−0.0163 (5)	0.359 (2)	0.041 (3)
F3	0.3530 (6)	0.0047 (7)	0.908 (2)		C18	0.0960 (5)	−0.0760 (5)	0.354 (2)	0.049 (3)
F4	0.4026 (7)	−0.0630 (8)	0.787 (3)		C19	0.0453 (5)	−0.0887 (6)	0.260 (2)	0.067 (4)
F5	0.3872 (7)	0.2750 (6)	0.776 (2)		C20	0.0183 (5)	−0.0431 (6)	0.172 (2)	0.066 (4)
F6	0.3255 (4)	0.2043 (7)	0.770 (3)		C21	0.0373 (6)	0.0143 (6)	0.169 (2)	0.064 (4)
F7	0.3281 (6)	0.2717 (9)	0.998 (3)		C22	0.0858 (5)	0.0287 (6)	0.267 (2)	0.058 (3)
F8	0.3906 (8)	0.2071 (7)	0.957 (3)		C23	0.1624 (5)	0.2641 (5)	0.600 (2)	0.044 (3)
N1	0.2400 (3)	0.1031 (4)	0.297 (1)		C24	0.2045 (5)	0.2682 (6)	0.737 (2)	0.055 (3)
N2	0.3985 (3)	0.0988 (5)	0.382 (1)		C25	0.2021 (5)	0.3182 (6)	0.856 (2)	0.061 (4)
C1	0.2354 (4)	0.0477 (5)	0.186 (2)	0.041 (3)	C26	0.1614 (6)	0.3591 (7)	0.845 (3)	0.078 (5)
C2	0.2351 (4)	−0.0085 (5)	0.308 (2)	0.045 (3)	C27	0.1186 (7)	0.3552 (7)	0.714 (3)	0.089 (5)
C3	0.2334 (4)	0.1579 (5)	0.167 (2)	0.042 (3)	C28	0.1208 (6)	0.3052 (7)	0.590 (2)	0.069 (4)
C4	0.2219 (4)	0.2159 (5)	0.277 (2)	0.046 (3)	C29	0.1005 (5)	0.2022 (5)	0.313 (2)	0.045 (3)
C5	0.2949 (4)	0.1076 (5)	0.399 (1)		C30	0.0533 (6)	0.1798 (7)	0.389 (2)	0.073 (4)
C6	0.3463 (5)	0.0986 (6)	0.275 (2)		C31	0.0017 (7)	0.1834 (8)	0.302 (3)	0.093 (5)
C7	0.4438 (7)	0.065 (1)	0.273 (3)		C32	−0.0022 (7)	0.2060 (7)	0.134 (3)	0.078 (5)
C8	0.465 (1)	0.098 (1)	0.129 (5)		C33	0.0421 (7)	0.2294 (8)	0.052 (3)	0.101 (6)
C9	0.4140 (6)	0.1633 (8)	0.443 (3)		C34	0.0949 (6)	0.2293 (7)	0.132 (2)	0.073 (4)
C10	0.4672 (7)	0.164 (1)	0.562 (3)		B1	0.3873 (8)	−0.006 (1)	0.770 (3)	
C11	0.1879 (4)	−0.0487 (5)	0.671 (2)	0.040 (3)	B2	0.3564 (7)	0.2396 (9)	0.874 (3)	

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.034 (1)	0.051 (1)	0.019 (1)	−0.001 (1)	0.000 (1)	−0.001 (1)
S	0.052 (2)	0.070 (2)	0.025 (1)	0.000 (1)	0.007 (1)	−0.001 (2)
P1	0.035 (1)	0.047 (1)	0.024 (1)	0.002 (1)	−0.003 (1)	−0.001 (1)
P2	0.038 (1)	0.045 (2)	0.030 (1)	−0.001 (1)	−0.003 (1)	0.001 (1)
F1	0.104 (7)	0.15 (1)	0.085 (7)	−0.014 (7)	−0.015 (7)	0.021 (7)
F2	0.16 (1)	0.33 (2)	0.15 (1)	−0.15 (1)	0.01 (1)	−0.07 (2)
F3	0.15 (1)	0.26 (2)	0.12 (1)	−0.02 (1)	0.043 (9)	−0.09 (1)
F4	0.27 (2)	0.25 (2)	0.18 (2)	0.12 (2)	0.03 (2)	0.11 (2)
F5	0.33 (2)	0.14 (1)	0.14 (1)	−0.08 (1)	0.08 (1)	0.02 (1)
F6	0.095 (8)	0.28 (2)	0.21 (2)	−0.029 (9)	0.004 (9)	−0.17 (1)
F7	0.16 (1)	0.33 (2)	0.23 (2)	−0.03 (1)	0.08 (1)	−0.19 (2)
F8	0.34 (2)	0.19 (1)	0.21 (2)	0.03 (2)	−0.15 (2)	0.01 (1)
N1	0.033 (4)	0.051 (5)	0.021 (4)	0.004 (4)	0.002 (4)	0.002 (4)
N2	0.026 (4)	0.094 (8)	0.041 (6)	−0.001 (5)	−0.001 (4)	−0.005 (6)
C5	0.035 (5)	0.062 (7)	0.020 (5)	0.001 (5)	−0.004 (4)	0.003 (6)
C6	0.043 (6)	0.094 (9)	0.020 (5)	−0.006 (7)	0.012 (5)	0.004 (7)
C7	0.059 (9)	0.20 (2)	0.05 (1)	−0.01 (1)	0.004 (8)	0.00 (1)
C8	0.14 (2)	0.29 (4)	0.13 (2)	0.09 (2)	0.01 (2)	−0.04 (3)
C9	0.059 (9)	0.14 (1)	0.09 (1)	−0.001 (9)	−0.005 (9)	−0.03 (1)
C10	0.07 (1)	0.24 (2)	0.09 (1)	−0.04 (1)	0.00 (1)	−0.06 (2)
B1	0.08 (1)	0.15 (2)	0.06 (1)	−0.02 (1)	−0.00 (1)	0.00 (1)
B2	0.06 (1)	0.09 (1)	0.08 (1)	−0.01 (1)	−0.02 (2)	0.00 (1)

[a] Standard deviations on the last significant digits are given in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$ and anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [b] z coordinate of Ni constrained to be fixed in the refinement (see text).

A further check on the correctness of the formula assigned to the n_2p_2 derivatives is provided by comparison with the complexes formed by the pnp ligand. Such a ligand differs from n_2p_2 merely in substitution of a CH_3 group for the terminal $-NEt_2$ group. In fact, the pnp complexes, obtained as tetraphenylborate salts, are 1:1 electrolytes (Table I), so they can be unambiguously assigned the formula $[Ni(SR)(pnp)]BPh_4$. Similarly, the complexes formed by the ligand ppp (which are also 1:1 electrolytes) have the formula $[Ni(SR)(ppp)]BPh_4$. All of these complexes must be assigned a square-planar coordination geometry, like that detected for $[Ni(SH)(n_2p_2H)](BF_4)_2$.

No band that could be attributed to the S–H stretching vibration has been detected in the IR spectra of any of these thiolo complexes. Indeed, this is rarely observed,[4] probably due to its low intensity. It was impossible to record the ^1H NMR spectra of these compounds, due to their low solubility and to the instability of the solutions.

The electronic spectra of the compounds are summarized in Table IV. The reflectance spectra are closely similar to the corresponding absorption spectra in nitroethane solution. They exhibit only minor changes due to substitution of the polydentate ligand or to replacement of H by CH_3 in the –SR group. Such spectra, showing no bands at frequencies <1.5 μm^{-1}, are typical of the square-planar nickel(II) complexes or of the low-spin square-pyramidal complexes, in which the metal atom undergoes a weak apical interaction.[16] On the basis of the structural results for the complex $[Ni(SH)(n_2p_2H)](BF_4)_2$ such weak interactions may be excluded in that case. In place of the single and intense band that is generally observed in the 1.5–2.5-μm^{-1} region in the spectra of the "regular" square-planar nickel(II) complexes, two bands close to each other are observed in the spectra of the present compounds. This is probably due to the fact that the symmetry of the ligand field is lower than D_{4h} as a consequence of geometric distortions and of the inhomogeneity of the donor set. It is now generally accepted that bands crowding in this region of the spectrum, for square-planar nickel(II) complexes, are due to transitions (in the strong-field limit) from the cluster of nonbonding one-electron levels a_{1g}, e_g, and b_{2g} to the strongly

Table III. Bond Lengths (Å) and Angles (deg) about the Metal Atom and Selected Values for the Cation[a]

Ni–S	2.144 (3)	Ni–P2	2.188 (3)
Ni–P1	2.190 (3)	Ni–N1	2.005 (8)
S–Ni–N1	170.1 (2)	S–Ni–P2	94.3 (1)
P1–Ni–P2	157.0 (1)	P1–Ni–N1	87.4 (3)
S–Ni–P1	93.3 (1)	P2–Ni–N1	88.8 (3)
P1–C2	1.83 (1)	N1–C3	1.52 (1)
P1–C11	1.84 (1)	N1–C5	1.51 (1)
P1–C17	1.81 (1)	N2–C6	1.47 (1)
P2–C4	1.79 (1)	C1–C2	1.51 (2)
P2–C23	1.85 (1)	C3–C4	1.52 (2)
P2–C29	1.79 (1)	C5–C6	1.53 (2)
N1–C1	1.46 (1)		
Ni–P1–C2	100.5 (4)	Ni–N1–C1	111.2 (6)
Ni–P1–C11	124.3 (4)	Ni–N1–C3	111.6 (6)
Ni–P1–C17	109.7 (4)	Ni–N1–C5	103.3 (6)
C2–P1–C11	108.2 (5)	C1–N1–C3	108.5 (8)
C2–P1–C17	106.2 (5)	C1–N1–C5	112.7 (8)
C11–P1–C17	106.6 (5)	C3–N1–C5	109.5 (8)
Ni–P2–C4	100.7 (4)	P1–C2–C1	104.7 (7)
Ni–P2–C23	126.4 (4)	P2–C4–C3	107.2 (8)
Ni–P2–C29	108.0 (4)	N1–C1–C2	111.3 (9)
C4–P2–C23	106.7 (5)	N1–C3–C4	111.3 (9)
C4–P2–C29	110.1 (6)	N1–C5–C6	114.3 (8)
C23–P2–C29	104.4 (5)	N2–C6–C5	112.4 (9)

[a] Esd's in parentheses.

Table IV. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compd	Absorption max,[a] μm^{-1} (ϵ_M for soln)
$[Ni(SH)(n_2p_2H)](BF_4)_2$	a: 1.85 sh, 2.32
	b: 1.85 sh, 2.35 (1145)
$[Ni(SCH_3)(n_2p_2H)](ClO_4)_2$	a: 1.68, 2.25
	b: 1.68 (333), 2.32 (1284)
$[Ni(SH)(pnp)]BPh_4$	a: 1.89, 2.47
	b: 1.89 sh, 2.41 (1115)
$[Ni(SCH_3)(pnp)]BPh_4$	a: 1.73, 2.41 sh
	b: 1.68 (234), 2.33 (1027)
$[Ni(SH)(ppp)]BPh_4$	a: 2.70 sh
	c: 2.70 sh
$[Ni(SCH_3)(ppp)]BPh_4$	a: 2.00 sh, 2.56 sh
	c: 2.00 sh, 2.56 sh

[a] Key: a, solid; b, nitroethane solution; c 1,2-dichloroethane solution.

antibonding level b_{1g}.[16] However, unambiguous assignments are difficult because the ordering of the nonbonding levels is expected to vary from case to case, as it is affected by various factors. A small blue shift of the bands is observed in the spectra of the ppp derivatives with respect to those of the other compounds.

The formation of –SR metal complexes has been attributed to the fact that HSR or H_2S releases one proton more easily when it is coordinated to a metal.[1,3] The phosphine ligands present in solution favor this process, acting as bases and forming phosphonium ions. In the case of the n_2p_2 ligand, one proton is captured by a nitrogen atom of the ligand which therefore becomes tridentate.

The stability, or scarce reactivity, of the thiolo complexes obtained in this and previous works[1,2] is surprisingly high compared to that of the few transition-metal thiolo derivatives that had been reported previously. Their stability must be attributed to various factors inherent in the nature of the polydentate ligands employed. First, such ligands bear numerous phenyl groups that shield the sulfur atom and prevent it from sharing its unused lone pairs with additional metal atoms: this process would favor the formation of sulfur clusters and it would ultimately lead to the formation of binary sulfides. Second, the peripheral positions of these ligands are predominantly occupied by phosphorus atoms which are able to compete with sulfur in forming strong covalent bonds to the metal. In fact, similarly shaped tripod ligands containing a preponderant number of "hard" donor atoms (as *N,N*-bis(2-diethylaminoethyl)-2′-diphenylphosphinoethylamine, set N_3P, and tris(2-dimethylaminoethyl)amine, set N_4) are unable to form thiolo complexes and to prevent the formation of the metal sulfides.[17] In the present square-planar complexes the sulfur atom is less effectively shielded than in the trigonal-bipyramidal ones. Evidently, the stability of the present compounds must be determined in part by the well-known electronic factors which favor the formation of the low-spin d^8 square-planar complexes. Additional factors, such as the formation of M–S π bonds, involving filled metal d orbitals and empty d orbitals on sulfur, may well contribute to the stability of all of these thiolo derivatives or to the reduction of their reactivity. However, such factors per se should favor even more strongly the formation of sulfur clusters or of metal sulfides.

Acknowledgment. Thanks are expressed to Mr. F. Cecconi and Mr. D. Masi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. $[Ni(SH)(n_2p_2H)](BF_4)_2$, 65120-48-1; $[Ni(SH)(n_2p_2H)](ClO_4)_2$, 65120-47-0; $[Ni(SH)(pnp)]BPh_4$, 65120-44-7; $[Ni(SH)(ppp)]BPh_4$, 65120-42-5; $[Ni(SCH_3)(n_2p_2H)](BF_4)_2$, 65120-40-3; $[Ni(SCH_3)(pnp)]BPh_4$, 65120-38-9; $[Ni(SCH_3)(ppp)]BPh_4$, 65120-36-7.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 1: M. Di Vaira, S. Midollini, and L. Sacconi, *Inorg. Chem.*, **16**, 1518 (1977).
(2) Part 2: C. Mealli, S. Midollini, and L. Sacconi, *Inorg. Chem.*, **17**, 632 (1978).
(3) C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, **98**, 689 (1976).
(4) J. P. Collman, R. K. Rothrock, and R. A. Stark, *Inorg. Chem.*, **16**, 437 (1977).
(5) B. H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, **14**, 322 (1975), and references therein.
(6) L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 2904 (1969).
(7) P. Dapporto, R. Morassi, and L. Sacconi, *J. Chem. Soc. A*, 1298 (1969).
(8) L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 2997 (1968); L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **7**, 1417 (1968).
(9) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(10) D. T. Cromer and J. A. Waber, *Acta Crystallogr.*, **18**, 104 (1965); R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(11) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(12) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964.
(13) Supplementary material.
(14) J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Am. Chem. Soc.*, **92**, 482 (1970).
(15) The effective symmetry of the ligand field, due to the distribution of negative charges about the metal atoms, may not coincide with that of the atomic centers. Interestingly, in the present case, as is indicated by the values of the Ni–P–C angles in Table III or by inspection of Figure 1, the electron pair shared by each phosphorus atom with the metal (this is expected to lie along a direction forming approximately equal angles with the directions of the P–C bonds) does not point toward the metal atom. A slightly "bent bond" results, such that the close electronic environment of the metal atom is more nearly planar than is the arrangement of the atomic centers.
(16) A. B. P. Lever, "Inorganic Electron Spectroscopy", Elsevier, Amsterdam, 1968, and references therein.
(17) Unpublished results of this laboratory.