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Synthesis, Properties, and X-Ray Characterization of 3d Metal–Mercapto and –Methylthio Complexes with the Poly(tertiary phosphines) Tris(2-diphenylphosphinoethyl)amine and Tris(2-diphenylphosphinoethyl)phosphine

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By reaction of hydrogen sulfide or methyl mercaptan with iron(II), cobalt(II), and nickel(II) aquo ions in the presence of the poly(tertiary phospine) ligands tris(2-diphenylphosphinoethyl)amine, np$_3$, and tris(2-diphenylphosphinoethyl)phosphine, pp$_3$, mercapto and methylthio complexes of the formula [M(SR)L]BPh$_4$ (R = H, CH$_3$) are formed. They are low spin with a five-coordinate trigonal-bipyramidal stereochemistry. The x-ray structures of the three isomorphous complexes [Fe(SH)(pp$_3$)]BPh$_4$ (I), [Co(SCH$_3$)(np$_3$)]BPh$_4$·(CH$_3$)$_2$CO (II), and [Ni(SH)(pp$_3$)]BPh$_4$ (III) are reported. The compounds crystallize in the triclinic $P\bar{1}$ space group, with two molecules per unit cell and with the following lattice constants: (I) a = 18.854 (25) Å, b = 16.467 (17) Å, c = 10.222 (9) Å, α = 94.13 (8)°, β = 95.66 (10)°, γ = 97.67 (11)°; (II) a = 18.626 (13) Å, b = 16.659 (10) Å, c = 10.096 (6) Å, α = 93.53 (5)°, β = 94.68 (6)°, γ = 98.15 (6)°; (III) a = 18.854 (8) Å, b = 16.440 (8) Å, c = 10.204 (4) Å, α = 94.36 (4)°, β = 95.83 (5)°, γ = 98.17 (6)°.

Introduction

As has been recently pointed out,[1] soluble metal complexes containing H$_2$S, SH$^-$, and S^{2-} as ligands are very rare, since they tend to revert to binary sulfides, which are the most stable and insoluble compounds.

Only two metal complexes with coordinated H$_2$S, having formulas [Ru(NH$_3$)$_5$(H$_2$S)](BF$_4$)$_2$[2] and W(CO)$_5$(H$_2$S),[3] have been isolated until now. Few mercapto complexes have been reported, among which are the following 3d metal derivatives: Mn$_2$(SH)$_2$(CO)$_8$, Ni(SH)(C$_5$H$_5$)(P(C$_4$H$_9$)$_3$), and [Cr(S-H)(H$_2$O)$_5$]SO$_4$.[4] The numerous compounds containing the S^{2-} ligand are generally polymeric. Only few examples of thio complexes of the types L$_n$M—S—ML$_n$ and L$_n$M≡S are known in transition metal chemistry[1] among which the nickel(II) complex with formula [(p$_3$)Ni—S—Ni(p$_3$)](BPh$_4$)$_2$,[5] where p$_3$ is the ligand 1,1,1-tris(diphenylphosphinomethyl)-ethane, constitutes the first example of a diamagnetic nickel(II) compound with a tetrahedral coordination.

The stability of these sulfur–metal complexes is certainly strongly influenced by the steric requirements of the ligands and by the nature of the donor atoms. They should be able to engage all of the metal orbitals in covalent σ and π bonds, thus preventing the formation of extra metal–sulfur and metal–metal bonds which in turn would lead to the formation of polymeric insoluble metal sulfides.

We have found that salts of divalent 3d metals like iron, cobalt, and nickel react with hydrogen sulfide in the presence of the potentially tetradentate tripod ligands tris(2-diphenylphosphinoethyl)phosphine, pp$_3$, or tris(2-diphenylphosphinoethyl)amine, np$_3$, forming stable monomeric mercapto complexes with the general formula [M(SH)L]BPh$_4$ (L = pp$_3$, M = Fe, Co, Ni; L = np$_3$, M = Co, Ni). The analogous methylthio complexes [M(SCH$_3$)L]BPh$_4$ have been obtained using CH$_3$SH as a reactant, in place of H$_2$S.

All complexes have been characterized by appropriate physical methods. The x-ray structures of the complexes [M(SH)(pp$_3$)]BPh$_4$ (M = Fe, Ni) and [Co(SCH$_3$)(np$_3$)]-BPh$_4$·(CH$_3$)$_2$CO have been determined.

Experimental Section

Reagents. All solvents were of reagent grade quality and were used without further purification. The ligand np$_3$ was prepared by the method previously described.[6] The ligand pp$_3$ was purchased from the Pressure Chemical Co., Pittsburgh, Pa., and was used without further purification.

Preparation of the Complexes. All reactions were carried out at room temperature under dry nitrogen atmosphere using deoxygenated solvents.

All of the compounds reported in Table I were prepared by the following procedure. The ligand (1 mmol) in 10 mL of acetone (or of DMF) was added at ambient temperature to a solution of the metal(II) tetrafluoroborate hexahydrate (1 mmol) in 30 mL of ethanol. Hydrogen sulfide (or methyl mercaptan) was bubbled into this solution until a definite, generally sudden, change of color took place. Addition of 1 mmol of sodium tetraphenylborate, dissolved in 10 mL of ethanol, led to precipitation of crystals which were filtered off, washed with ethanol first and then with petroleum ether, and were finally dried in a current of nitrogen.

Attempts to prepare the np$_3$ iron derivatives by the above procedure failed, as precipitation of the metal sulfide took place.

The analytical data for the complexes are listed in Table I.

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recording of the UV–visible spectra have been described previously.[7]

Collection and Reduction of X-Ray Intensity Data. Data were collected following essentially the same procedure for the complexes [Fe(SH)(pp$_3$)]BPh$_4$ (I), [Co(SCH$_3$)(np$_3$)]BPh$_4$·(CH$_3$)$_2$CO (II), and [Ni(SH)(pp$_3$)]BPh$_4$ (III). The analogous mercaptocobalt complex could not be investigated because suitable crystals were not obtained. Details of crystal data and intensity collection are reported in Table II. The three compounds are isomorphous to each other and belong to the triclinic system; the centric space group $P\bar{1}$ was initially assumed

Table I. Analytical and Physical Data for the Complexes

Compd	Color	% C Calcd	% C Found	% H Calcd	% H Found	% metal Calcd	% metal Found	μ_{eff}(293 K), μ_B	Λ_M,[a] cm^2 Ω^{-1} mol^{-1}
[Fe(SH)(pp$_3$)]BPh$_4$	Garnet red	73.48	73.37	5.89	6.01	5.17	4.85	3.06	49
[Fe(SCH$_3$)(pp$_3$)]BPh$_4$	Olive	73.64	72.90	6.00	6.40	5.11	4.85	3.31	47
[Co(SH)(pp$_3$)]BPh$_4$	Green	73.30	73.55	5.87	6.28	5.45	4.58	2.06	49
[Co(SCH$_3$)(pp$_3$)]BPh$_4$[b]	Brown	73.43	73.42	5.98	5.98	5.38	5.42	2.03	49
[Co(np$_3$)]BPh$_4$[c]	Brown	74.46	73.76	5.97	6.25	5.54	5.20	2.12	48
[Co(SCH$_3$)(np$_3$)]BPh$_4$·(CH$_3$)$_2$CO[d]	Amaranth	73.90	74.27	6.30	5.93	5.18	5.45	2.05	48
[Ni(SH)(pp$_3$)]BPh$_4$[e]	Dark brown	73.31	72.91	5.87	5.82	5.43	5.10	Diam	45
[Ni(SCH$_3$)(pp$_3$)]BPh$_4$	Dark green	73.44	74.54	5.98	6.05	5.36	5.25	Diam	47
[Ni(SH)(np$_3$)]BPh$_4$[f]	Blue	74.48	74.12	5.97	6.13	5.52	5.30	Diam	47
[Ni(SCH$_3$)(np$_3$)]BPh$_4$[g]	Purple	74.60	74.68	6.07	6.33	5.44	5.20	Diam	47

[a] Molar conductance values for 10^{-3} M nitroethane solution. [b] Calcd: S, 2.93. Found: S, 3.07. [c] Calcd: N, 1.32; S, 3.01. Found: N, 1.35; S, 3.43. [d] Calcd: N, 1.23. Found: N, 1.28. [e] Calcd: S, 2.97. Found: S, 2.85. [f] Calcd: N, 1.32. Found: N, 1.37. [g] Calcd: N, 1.30. Found: N, 1.23.

Table II. Summary of Crystal Data, Intensity Collection Method, and Refinement

	[Fe(SH)(pp$_3$)]BPh$_4$	[Co(SCH$_3$)(np$_3$)]BPh$_4$·(CH$_3$)$_2$CO	[Ni(SH)(pp$_3$)]BPh$_4$
Formula	C$_{66}$H$_{63}$B$_1$Fe$_1$P$_4$S$_1$	C$_{70}$H$_{72}$B$_1$Co$_1$N$_1$O$_1$P$_3$S$_1$	C$_{66}$H$_{63}$B$_1$Ni$_1$P$_4$S$_1$
Mol wt	1078.85	1138.09	1081.72
a, Å	18.854 (25)	18.626 (13)	18.854 (8)
b, Å	16.467 (17)	16.659 (10)	16.440 (8)
c, Å	10.222 (9)	10.096 (6)	10.204 (4)
α, deg	94.13 (8)	93.53 (5)	94.36 (4)
β, deg	95.66 (10)	94.68 (6)	95.83 (5)
γ, deg	97.67 (11)	98.15 (6)	98.17 (6)
V, Å^3	3118.2	3082.2	3101.4
Z	2	2	2
Density, g cm^{-3}	1.149 (calcd)	1.226 (calcd)	1.158 (calcd)
	1.15 (exptl, by flotation)	1.24(exptl)	1.15(exptl)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal dimensions, mm	0.33 × 0.23 × 0.80	0.07 × 0.10 × 0.40	0.07 × 0.13 × 0.70
Crystal shape	Needles, [001] elongated	Prisms, [001] elongated	Needles, [001] elongated
Radiation	Mo Kα(λ 0.7107 Å), graphite monochromatized	Mo Kα	MoKα
Temp, °C	24	24	24
μ, cm^{-1}	4.09	4.27	4.83
Transmission factors	0.865-0.972	0.960-0.990	0.930-0.990
Takeoff angle, deg	4	4	4
Scan speed, 2ϑ deg/min	4.0	2.4	3.0
Scan range, deg	1.00, symmetric	0.80, symmetric	0.80, symmetric
Background counting	$t_{b_1} = t_{b_2} = {}^{1}/_2 t_s$ (t_s = total scan time)	$t_{b_1} = t_{b_2} = {}^{1}/_2 t_s$	$t_{b_1} = t_{b_2} = {}^{1}/_2 t_s$
2ϑ limits, deg	4.0-45.0	4.0-40.0	4.0-48.0
Final no. of variables	323	339	323
Unique data used ($F_o^2 > 3\sigma(F_o^2)$)	2816	2120	3675
Error in observation of unit wt, electrons	2.5	1.6	1.9
R	9.1	6.9	7.9
R_w	10.7	8.4	8.6

and the choice was confirmed by subsequent structure determination. Lattice constants were determined by least-squares refinement of the angular positions of 30 reflections for each compound. The crystal of the iron complex was sealed in a capillary tube, as the compound decomposes rapidly in air, under exposure to the x rays. The intensities of three standard reflections, measured every 100 min, showed a linear decrease (ca. 10% in total) for the iron complex and showed no systematic trend for the other two compounds. Data for the iron derivative were properly rescaled to account for decomposition. Data sets were processed in the usual way with $\sigma(F_o^2)$ calculated using a value of 0.04 for p.[8] Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. Corrections for absorption were applied.[9]

Solution and Refinement of the Structures. The structure of the nickel compound (III) was solved first, by standard heavy-atom techniques. All nonhydrogen atom positions were located by a series of Fourier syntheses. Full-matrix least-squares refinement was undertaken, in which the function $\sum w(|F_o| - |F_c|)^2$ was minimized, with weights $w = 1/\sigma^2(F_o)$. Anisotropic thermal parameters were used for atoms in the coordination polyhedron and isotropic parameters for the boron and carbon atoms. Hydrogen atoms 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.[9] Atomic scattering factors were taken from ref 10 and anomalous dispersion terms for the metal, phosphorus, and sulfur atoms were included in F_c.[11] Refinement converged to the R and R_w values of 0.079 and 0.086, respectively; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. A final ΔF Fourier showed no peak having height higher than one-sixth that of a carbon atom, measured from a ΔF Fourier calculated without contribution from that carbon atom. Values of the ΔF function in a shell close to the sulfur atom position were positive, but there was no clear indication of the SH hydrogen atom position. Indeed, this would be expected to be affected by disorder.

The structure of the iron compound (I) was refined following the same procedure as for the nickel isomorph, using atomic coordinates from the structure of the nickel compound as input. Refinement converged to the R and R_w values of 0.091 and 0.107, respectively. These are higher than for the nickel compound, probably due to the quality of the data, affected by decomposition.

Refinement of the structure of the cobalt compound (II) also used atomic coordinates from the structure of the nickel isomorph as input, accounting for the change of the nature of the central donor atom of the ligand molecule. A damping factor for parameter shifts was applied during preliminary cycles in this case. A Fourier map

Table III. Atomic Parameters for [Fe(SH)(pp$_3$)]BPh$_4$^{a}

	x	y	z	U, Å^2		x	y	z	U, Å^2
Fe	0.2191 (1)	0.1600 (2)	0.3257 (2)		C32	0.284 (1)	0.396 (1)	0.606 (2)	0.117 (8)
S	0.1087 (3)	0.1765 (3)	0.2361 (5)		C33	0.302 (1)	0.483 (2)	0.595 (3)	0.152 (9)
P1	0.2082 (2)	0.0160 (3)	0.3149 (4)		C34	0.278 (1)	0.517 (1)	0.480 (3)	0.128 (9)
P2	0.2855 (3)	0.2194 (3)	0.1669 (5)		C35	0.239 (1)	0.468 (1)	0.385 (2)	0.101 (7)
P3	0.2168 (2)	0.2414 (3)	0.5211 (4)		C36	0.219 (1)	0.383 (1)	0.395 (2)	0.090 (6)
P4	0.3283 (2)	0.1487 (3)	0.4202 (4)		C37	0.134 (1)	0.238 (1)	0.598 (2)	0.072 (6)
C1	0.340 (1)	0.045 (1)	0.451 (2)	0.068 (5)	C38	0.121 (1)	0.185 (1)	0.702 (2)	0.103 (7)
C2	0.298 (1)	−0.012 (1)	0.339 (2)	0.067 (5)	C39	0.055 (1)	0.180 (1)	0.759 (2)	0.117 (8)
C3	0.401 (1)	0.181 (1)	0.319 (2)	0.074 (6)	C40	0.006 (1)	0.228 (1)	0.721 (2)	0.109 (8)
C4	0.377 (1)	0.251 (1)	0.240 (2)	0.074 (6)	C41	0.016 (1)	0.283 (1)	0.616 (2)	0.132 (9)
C5	0.353 (1)	0.209 (1)	0.581 (2)	0.076 (6)	C42	0.085 (1)	0.290 (1)	0.562 (2)	0.091 (6)
C6	0.284 (1)	0.213 (1)	0.645 (2)	0.064 (5)	C43	0.552 (1)	0.322 (1)	0.740 (2)	0.063 (5)
C7	0.163 (1)	−0.031 (1)	0.452 (2)	0.062 (5)	C44	0.493 (1)	0.297 (1)	0.810 (2)	0.068 (5)
C8	0.112 (1)	0.010 (1)	0.501 (2)	0.091 (7)	C45	0.451 (1)	0.353 (1)	0.859 (2)	0.084 (6)
C9	0.071 (1)	−0.032 (1)	0.598 (2)	0.121 (8)	C46	0.465 (1)	0.435 (1)	0.845 (2)	0.095 (7)
C10	0.085 (1)	−0.105 (1)	0.626 (2)	0.109 (7)	C47	0.522 (1)	0.461 (1)	0.784 (2)	0.104 (8)
C11	0.136 (1)	−0.146 (1)	0.586 (2)	0.125 (9)	C48	0.563 (1)	0.406 (1)	0.736 (2)	0.082 (6)
C12	0.178 (1)	−0.107 (1)	0.482 (2)	0.107 (7)	C49	0.686 (1)	0.295 (1)	0.726 (2)	0.073 (6)
C13	0.164 (1)	−0.052 (1)	0.170 (2)	0.059 (5)	C50	0.707 (1)	0.331 (1)	0.851 (2)	0.095 (7)
C14	0.094 (1)	−0.041 (1)	0.125 (2)	0.075 (6)	C51	0.781 (1)	0.357 (1)	0.894 (2)	0.116 (8)
C15	0.055 (1)	−0.094 (1)	0.021 (2)	0.088 (6)	C52	0.830 (1)	0.350 (1)	0.817 (2)	0.112 (8)
C16	0.086 (1)	−0.156 (1)	−0.026 (2)	0.096 (7)	C53	0.814 (7)	0.317 (1)	0.691 (2)	0.122 (8)
C17	0.153 (1)	−0.167 (1)	0.013 (2)	0.114 (8)	C54	0.741 (1)	0.287 (1)	0.643 (2)	0.099 (7)
C18	0.193 (1)	−0.115 (1)	0.114 (2)	0.082 (6)	C55	0.578 (1)	0.168 (1)	0.724 (2)	0.058 (5)
C19	0.292 (1)	0.144 (1)	0.030 (2)	0.056 (5)	C56	0.605 (1)	0.149 (1)	0.858 (1)	0.073 (6)
C20	0.231 (1)	0.092 (1)	−0.017 (2)	0.070 (6)	C57	0.582 (1)	0.073 (1)	0.900 (2)	0.069 (5)
C21	0.229 (1)	0.027 (1)	−0.123 (2)	0.091 (7)	C58	0.536 (1)	0.015 (1)	0.830 (2)	0.070 (6)
C22	0.294 (1)	0.021 (1)	−0.174 (2)	0.090 (7)	C59	0.508 (1)	0.027 (1)	0.698 (2)	0.067 (5)
C23	0.352 (1)	0.073 (1)	−0.131 (2)	0.085 (6)	C60	0.530 (1)	0.105 (1)	0.656 (2)	0.055 (5)
C24	0.358 (1)	0.137 (1)	−0.025 (2)	0.088 (6)	C61	0.590 (1)	0.257 (1)	0.504 (2)	0.058 (5)
C25	0.262 (1)	0.308 (1)	0.079 (2)	0.071 (6)	C62	0.612 (1)	0.194 (1)	0.433 (2)	0.075 (6)
C26	0.307 (1)	0.382 (1)	0.097 (2)	0.082 (6)	C63	0.611 (1)	0.189 (1)	0.290 (2)	0.098 (7)
C27	0.288 (1)	0.450 (1)	0.029 (2)	0.121 (8)	C64	0.585 (1)	0.253 (1)	0.233 (2)	0.087 (6)
C28	0.226 (1)	0.437 (1)	−0.052 (2)	0.111 (8)	C65	0.563 (1)	0.315 (1)	0.298 (2)	0.074 (6)
C29	0.176 (1)	0.366 (1)	−0.068 (2)	0.118 (7)	C66	0.564 (1)	0.320 (1)	0.442 (2)	0.071 (6)
C30	0.196 (1)	0.298 (1)	0.001 (2)	0.102 (7)	B	0.600 (1)	0.260 (1)	0.678 (2)	0.057 (6)
C31	0.242 (1)	0.348 (1)	0.506 (2)	0.070 (6)					

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.054 (2)	0.082 (2)	0.034 (1)	0.004 (1)	0.007 (1)	0.017 (1)
S	0.061 (4)	0.131 (5)	0.071 (4)	0.025 (3)	−0.010 (3)	0.012 (4)
P1	0.059 (3)	0.079 (4)	0.036 (3)	0.005 (3)	0.007 (2)	0.015 (3)
P2	0.058 (3)	0.086 (4)	0.051 (3)	0.002 (3)	0.011 (3)	0.027 (3)
P3	0.067 (3)	0.078 (4)	0.034 (3)	0.006 (3)	0.006 (2)	0.015 (3)
P4	0.049 (3)	0.079 (4)	0.049 (3)	0.006 (3)	0.003 (3)	0.013 (3)

^{a} In this and subsequent tables of atomic parameters, standard deviations on the last significant digit are given in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2 U((\sin^2 \vartheta)/\lambda^2)]$ and anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$; these forms are used throughout.

calculated at R = ca. 0.11 clearly showed the position of the −SCH$_3$ carbon atom. Fixed hydrogen atom contributions were applied, as described above. The methyl hydrogen atom positions, located from a ΔF Fourier calculated at a later stage of refinement (R = ca. 0.08), were optimized by a least-squares procedure[9] and introduced in subsequent calculations without further change in their positions. The difference Fourier also showed one molecule of acetone in the asymmetric unit, consistent with observation of the CO stretching frequency in the IR spectrum of the solid and with the measured density value (Table II). The solvent position was affected by disorder: there were three equidistant resolved peaks in the map, indicating that the acetone molecule was probably distributed between three positions approximately related by 120° rotations about an axis perpendicular to the molecular plane. A four-atom model was initially consided for the molecule of the solvent, formed by three carbon atoms arranged as the three maxima in the ΔF Fourier and by a fourth carbon atom placed in the barycenter of the triangle formed by the previous three (the difference map showed diffuse positive density in this region). After a set of least-squares cycles on atoms of the solvent, the temperature factor of the central atom and the esd's on its coordinates were extremely high. That atom was then excluded from the model. Refinement of parameters of the three "atoms" from the ΔF Fourier was then undertaken, assigning the carbon form factor and unit population parameters (in agreement with the measured density value). A set of cycles yielded high-temperature factors for the solvent and an arrangement consistent with the overall dimensions of the acetone

molecule. There were no contacts below ca. 3.4 Å between the solvent and nonhydrogen atoms in the structure. R was 0.071 at this point. Values of the parameters of the solvent from this refinement were not allowed to change during subsequent cycles, that were performed with the same procedure as that followed for the other two compounds. Convergence was attained at R = 0.069 and R_w = 0.084. The average shift:error ratio was <0.25 at the end of the refinement, for all of the compounds.

The final positional and thermal parameters appear in Tables III–V. A listing of the observed and calculated structure amplitudes is available.[12]

Results and Discussion

As it is well-known, by action of H$_2$S on solutions of transition metal salts, insoluble polymeric metal sulfides are generally obtained, even in presence of strongly coordinating ligands. However if the solutions of the iron(II), cobalt(II), or nickel(II) ions contain the tertiary phosphines here considered, reaction with H$_2$S or CH$_3$SH yields complex ions with the general formula [M(SR)L]$^+$ (R = H, CH$_3$).

In previous research we have found that the organic solutions of [M(H$_2$O)$_6$](BF$_4$)$_2$ salts (M = Co, Ni) and of the ligands np$_3$ or pp$_3$ contain high concentrations of five-coordinated aquo and hydroxo complexes, having the general formulas [M-(H$_2$O)L]$^{2+}$ and [M(OH)L]$^+$.[13] Many of such compounds have

Table IV. Atomic Parameters for [Co(SCH$_3$)(np$_3$)]BPh$_4$·(CH$_3$)$_2$CO

	x	y	z	U, Å^2		x	y	z	U, Å^2
Co	0.2208 (1)	0.1581 (1)	0.3303 (2)		C34	0.293 (1)	0.525 (1)	0.501 (2)	0.084 (6)
S	0.1093 (2)	0.1511 (3)	0.2395 (5)		C35	0.253 (1)	0.484 (1)	0.397 (2)	0.074 (6)
P1	0.2080 (2)	0.0191 (3)	0.3081 (4)		C36	0.232 (1)	0.400 (1)	0.397 (1)	0.059 (5)
P2	0.2801 (2)	0.2150 (3)	0.1668 (4)		C37	0.135 (1)	0.246 (1)	0.595 (1)	0.044 (4)
P3	0.2166 (2)	0.2496 (3)	0.5047 (4)		C38	0.118 (1)	0.185 (1)	0.681 (2)	0.072 (5)
N	0.3274 (6)	0.1503 (7)	0.4184 (9)		C39	0.054 (1)	0.181 (1)	0.746 (2)	0.087 (6)
C1	0.333 (1)	0.067 (1)	0.457 (1)	0.047 (5)	C40	0.008 (1)	0.236 (1)	0.723 (2)	0.085 (6)
C2	0.300 (1)	0.001 (1)	0.347 (1)	0.057 (5)	C41	0.024 (1)	0.298 (1)	0.644 (2)	0.089 (6)
C3	0.387 (1)	0.172 (1)	0.327 (1)	0.053 (5)	C42	0.089 (1)	0.304 (1)	0.576 (2)	0.074 (6)
C4	0.371 (1)	0.243 (1)	0.250 (1)	0.053 (5)	C43	0.081 (1)	0.248 (1)	0.230 (2)	0.081 (6)
C5	0.348 (1)	0.205 (1)	0.543 (1)	0.053 (5)	C44	0.545 (1)	0.317 (1)	0.739 (1)	0.048 (5)
C6	0.282 (1)	0.211 (1)	0.619 (1)	0.059 (5)	C45	0.485 (1)	0.290 (1)	0.805 (2)	0.062 (5)
C7	0.160 (1)	−0.031 (1)	0.437 (1)	0.053 (5)	C46	0.441 (1)	0.341 (1)	0.864 (2)	0.070 (7)
C8	0.111 (1)	0.008 (1)	0.500 (2)	0.065 (5)	C47	0.461 (1)	0.423 (1)	0.856 (2)	0.077 (6)
C9	0.069 (1)	−0.034 (1)	0.594 (2)	0.082 (6)	C48	0.518 (1)	0.454 (1)	0.794 (2)	0.079 (6)
C10	0.080 (1)	−0.108 (1)	0.624 (2)	0.080 (6)	C49	0.561 (1)	0.401 (1)	0.737 (1)	0.064 (5)
C11	0.729 (1)	−0.145 (1)	0.564 (2)	0.098 (7)	C50	0.682 (1)	0.292 (1)	0.723 (2)	0.056 (5)
C12	0.170 (1)	−0.107 (1)	0.468 (2)	0.087 (6)	C51	0.704 (1)	0.329 (1)	0.847 (2)	0.076 (6)
C13	0.173 (1)	−0.051 (1)	0.167 (1)	0.047 (5)	C52	0.778 (1)	0.356 (1)	0.897 (2)	0.091 (6)
C14	0.101 (1)	−0.052 (1)	0.111 (1)	0.064 (5)	C53	0.829 (1)	0.347 (1)	0.814 (2)	0.083 (6)
C15	0.071 (1)	−0.109 (1)	0.005 (2)	0.068 (5)	C54	0.811 (1)	0.313 (1)	0.690 (2)	0.096 (7)
C16	0.113 (1)	−0.163 (1)	−0.044 (2)	0.077 (6)	C55	0.739 (1)	0.284 (1)	0.643 (2)	0.077 (6)
C17	0.182 (1)	−0.163 (1)	0.008 (2)	0.088 (6)	C56	0.576 (1)	0.164 (1)	0.722 (1)	0.040 (4)
C18	0.214 (1)	−0.106 (1)	0.114 (2)	0.066 (5)	C57	0.598 (1)	0.145 (1)	0.850 (2)	0.062 (5)
C19	0.289 (1)	0.145 (1)	0.032 (1)	0.040 (4)	C58	0.580 (1)	0.070 (1)	0.901 (1)	0.055 (5)
C20	0.229 (1)	0.093 (1)	−0.030 (1)	0.060 (5)	C59	0.533 (1)	0.011 (1)	0.819 (1)	0.059 (5)
C21	0.232 (1)	0.037 (1)	−0.136 (2)	0.075 (6)	C60	0.509 (1)	0.027 (1)	0.697 (2)	0.055 (5)
C22	0.300 (1)	0.031 (1)	−0.180 (2)	0.072 (6)	C61	0.531 (1)	0.102 (1)	0.646 (1)	0.046 (5)
C23	0.358 (1)	0.079 (1)	−0.127 (2)	0.072 (5)	C62	0.586 (1)	0.255 (1)	0.508 (1)	0.050 (5)
C24	0.355 (1)	0.136 (1)	−0.025 (2)	0.063 (5)	C63	0.612 (1)	0.194 (1)	0.426 (2)	0.063 (5)
C25	0.262 (1)	0.302 (1)	0.084 (1)	0.047 (5)	C64	0.607 (1)	0.193 (1)	0.284 (2)	0.074 (6)
C26	0.304 (1)	0.376 (1)	0.107 (2)	0.069 (5)	C65	0.579 (1)	0.255 (1)	0.225 (2)	0.086 (6)
C27	0.288 (1)	0.447 (1)	0.038 (2)	0.089 (6)	C66	0.553 (1)	0.314 (1)	0.301 (2)	0.074 (6)
C28	0.229 (1)	0.439 (1)	−0.047 (2)	0.094 (7)	C67	0.557 (1)	0.313 (1)	0.438 (2)	0.059 (5)
C29	0.185 (1)	0.366 (1)	−0.074 (2)	0.108 (7)	C68[a]	0.908	0.327	0.279	0.425
C30	0.204 (1)	0.295 (1)	−0.009 (2)	0.090 (6)	C69[a]	0.907	0.436	0.345	0.400
C31	0.249 (1)	0.355 (1)	0.505 (2)	0.046 (5)	C70[a]	0.804	0.350	0.273	0.561
C32	0.289 (1)	0.398 (1)	0.612 (2)	0.099 (7)	B	0.598 (1)	0.257 (1)	0.667 (2)	0.048 (5)
C33	0.311 (1)	0.484 (2)	0.613 (2)	0.127 (8)					

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.035 (2)	0.041 (2)	0.044 (2)	0.003 (1)	0.006 (1)	0.008 (1)
S	0.042 (3)	0.052 (3)	0.074 (4)	0.009 (3)	0.000 (3)	0.002 (3)
P1	0.034 (3)	0.043 (3)	0.047 (3)	0.002 (2)	0.006 (2)	0.004 (3)
P2	0.039 (3)	0.044 (3)	0.042 (3)	0.002 (3)	0.004 (2)	0.012 (3)
P3	0.040 (3)	0.040 (3)	0.047 (3)	0.007 (2)	0.003 (3)	0.008 (3)
N	0.046 (9)	0.035 (9)	0.041 (9)	0.001 (7)	0.001 (7)	0.001 (7)

[a] Atoms of the solvent molecule, not refined during the last set of cycles (see text); the esd's on positional parameters of these atoms are <0.01.

been isolated. The x-ray diffraction studies of two of these, namely, the [Co(H$_2$O)(pp$_3$)](BF$_4$)$_2$ and the [Co(OH)-(pp$_3$)]BF$_4$ complexes, have revealed that both possess a distorted trigonal-bipyramidal geometry.[13]
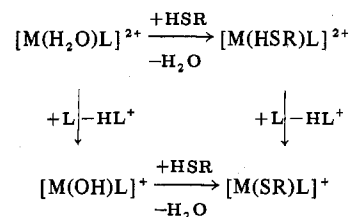
In view of the above results, we can assume that the formation of the mercapto and methylthio complexes proceeds through the reaction of H$_2$S or CH$_3$SH with such complex cations, according to Scheme I.

The facile formation of the [M(SR)L]$^+$ species as final compounds is accounted for by the considerable acidity assumed by H$_2$S and CH$_3$SH upon coordination.[2,3] Also the basicity of the tertiary phosphine groups of the ligands should play a role in stabilizing the deprotonated species through the formation of quaternary phosphonium ions.

All [M(SR)L]BPh$_4$ complexes are stable under inert-gas atmosphere; the nickel compounds are fairly stable also in air. The complexes are soluble in polar organic solvents and behave as 1:1 electrolytes in nitroethane (Table I). They slowly decompose in hot solutions.

All compounds are low spin, with room-temperature μ_{eff} values (Table I) corresponding to a triplet ground state for the iron derivatives (3.06–3.31 μ_B), a doublet ground state for

Scheme I

$$[M(H_2O)L]^{2+} \xrightarrow[-H_2O]{+HSR} [M(HSR)L]^{2+}$$

$$+L\bigg|-HL^+ \qquad\qquad +L\bigg|-HL^+$$

$$[M(OH)L]^+ \xrightarrow[-H_2O]{+HSR} [M(SR)L]^+$$

the cobalt derivatives (2.03–2.12 μ_B), and a singlet for the nickel ones.

The structures of the three compounds investigated by x-ray techniques consist of [M(SR)L]$^+$ cations and of BPh$_4$$^-$ anions. In the lattice of the cobalt compound there are in addition interspersed acetone molecules from the solvent.

The coordination geometry of the three complexes is essentially trigonal bipyramidal, with the three peripheral phosphorus atoms of the ligand lying in the equatorial plane. The axial positions of the bipyramid are occupied by the central donor atom of the ligand molecule and by the sulfur atom. The same type of coordination may be assigned to all complexes of this series, on the basis of their magnetic and

Table V. Atomic Parameters for [Ni(SH)(pp₃)]BPh₄

	x	y	z	U, Å²		x	y	z	U, Å²
Ni	0.2248 (1)	0.1577 (1)	0.3306 (1)		C32	0.284 (1)	0.397 (1)	0.610 (1)	0.095 (5)
S	0.1133 (2)	0.1728 (2)	0.2424 (3)		C33	0.302 (1)	0.485 (1)	0.597 (1)	0.121 (6)
P1	0.2074 (2)	0.0159 (2)	0.3112 (3)		C34	0.278 (1)	0.514 (1)	0.480 (1)	0.103 (5)
P2	0.2834 (2)	0.2155 (2)	0.1663 (3)		C35	0.240 (1)	0.468 (1)	0.380 (1)	0.085 (4)
P3	0.2173 (2)	0.2378 (2)	0.5152 (3)		C36	0.222 (1)	0.382 (1)	0.388 (1)	0.071 (4)
P4	0.3312 (2)	0.1478 (2)	0.4220 (3)		C37	0.135 (1)	0.233 (1)	0.595 (1)	0.053 (3)
C1	0.340 (1)	0.042 (1)	0.449 (1)	0.052 (3)	C38	0.119 (1)	0.178 (1)	0.688 (1)	0.082 (4)
C2	0.297 (1)	−0.013 (1)	0.332 (1)	0.058 (3)	C39	0.054 (1)	0.176 (1)	0.744 (1)	0.099 (5)
C3	0.401 (1)	0.180 (1)	0.318 (1)	0.057 (3)	C40	0.007 (1)	0.227 (1)	0.709 (1)	0.090 (5)
C4	0.377 (1)	0.250 (1)	0.241 (1)	0.063 (4)	C41	0.018 (1)	0.282 (1)	0.617 (1)	0.100 (5)
C5	0.353 (1)	0.208 (1)	0.580 (1)	0.060 (3)	C42	0.085 (1)	0.286 (1)	0.558 (1)	0.076 (4)
C6	0.284 (1)	0.212 (1)	0.643 (1)	0.052 (3)	C43	0.551 (1)	0.323 (1)	0.745 (1)	0.052 (3)
C7	0.163 (1)	−0.032 (1)	0.441 (1)	0.055 (3)	C44	0.493 (1)	0.296 (1)	0.812 (1)	0.059 (3)
C8	0.112 (1)	0.004 (1)	0.498 (1)	0.073 (4)	C45	0.450 (1)	0.350 (1)	0.867 (1)	0.065 (4)
C9	0.072 (1)	−0.036 (1)	0.592 (1)	0.092 (5)	C46	0.465 (1)	0.433 (1)	0.853 (1)	0.084 (4)
C10	0.087 (1)	−0.111 (1)	0.625 (1)	0.092 (5)	C47	0.522 (1)	0.461 (1)	0.790 (1)	0.095 (5)
C11	0.139 (1)	−0.150 (1)	0.575 (1)	0.105 (5)	C48	0.566 (1)	0.407 (1)	0.740 (1)	0.075 (4)
C12	0.178 (1)	−0.110 (1)	0.478 (1)	0.086 (4)	C49	0.687 (1)	0.294 (1)	0.728 (1)	0.060 (4)
C13	0.162 (1)	−0.051 (1)	0.170 (1)	0.050 (3)	C50	0.708 (1)	0.330 (1)	0.857 (1)	0.090 (5)
C14	0.091 (1)	−0.043 (1)	0.123 (1)	0.061 (3)	C51	0.784 (1)	0.359 (1)	0.908 (1)	0.110 (5)
C15	0.052 (1)	−0.096 (1)	0.017 (1)	0.082 (4)	C52	0.832 (1)	0.351 (1)	0.819 (2)	0.099 (5)
C16	0.082 (1)	−0.158 (1)	−0.034 (1)	0.088 (5)	C53	0.815 (1)	0.318 (1)	0.695 (1)	0.103 (5)
C17	0.150 (1)	−0.169 (1)	0.004 (1)	0.096 (5)	C54	0.743 (1)	0.290 (1)	0.652 (1)	0.075 (4)
C18	0.191 (1)	−0.115 (1)	0.112 (1)	0.080 (4)	C55	0.579 (1)	0.167 (1)	0.728 (1)	0.053 (3)
C19	0.289 (1)	0.141 (1)	0.027 (1)	0.050 (3)	C56	0.605 (1)	0.148 (1)	0.855 (1)	0.063 (4)
C20	0.229 (1)	0.087 (1)	−0.022 (1)	0.058 (3)	C57	0.581 (1)	0.073 (1)	0.902 (1)	0.066 (4)
C21	0.228 (1)	0.025 (1)	−0.127 (1)	0.080 (4)	C58	0.534 (1)	0.014 (1)	0.825 (1)	0.065 (4)
C22	0.293 (1)	0.019 (1)	−0.179 (1)	0.082 (4)	C59	0.508 (1)	0.029 (1)	0.700 (1)	0.055 (3)
C23	0.353 (1)	0.072 (1)	−0.133 (1)	0.083 (4)	C60	0.529 (1)	0.105 (1)	0.653 (1)	0.052 (3)
C24	0.355 (1)	0.134 (1)	−0.027 (1)	0.075 (4)	C61	0.590 (1)	0.258 (1)	0.516 (1)	0.052 (3)
C25	0.258 (1)	0.303 (1)	0.079 (1)	0.050 (3)	C62	0.614 (1)	0.193 (1)	0.436 (1)	0.066 (4)
C26	0.302 (1)	0.377 (1)	0.095 (1)	0.068 (4)	C63	0.609 (1)	0.193 (1)	0.294 (1)	0.083 (4)
C27	0.284 (1)	0.443 (1)	0.025 (1)	0.093 (5)	C64	0.584 (1)	0.255 (1)	0.233 (1)	0.084 (4)
C28	0.222 (1)	0.431 (1)	−0.057 (1)	0.094 (5)	C65	0.562 (1)	0.316 (1)	0.307 (1)	0.069 (4)
C29	0.173 (1)	0.357 (1)	−0.073 (1)	0.106 (5)	C66	0.564 (1)	0.319 (1)	0.444 (1)	0.062 (4)
C30	0.195 (1)	0.290 (1)	−0.001 (1)	0.079 (4)	B	0.602 (1)	0.261 (1)	0.679 (1)	0.050 (4)
C31	0.244 (1)	0.347 (1)	0.501 (1)	0.054 (3)					

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.037 (1)	0.049 (1)	0.044 (1)	0.006 (1)	0.002 (1)	0.006 (1)
S	0.044 (2)	0.093 (3)	0.070 (3)	0.018 (2)	−0.011 (2)	0.004 (2)
P1	0.045 (2)	0.043 (2)	0.047 (2)	0.006 (2)	0.005 (2)	0.008 (2)
P2	0.044 (2)	0.051 (2)	0.050 (2)	0.005 (2)	0.009 (2)	0.013 (2)
P3	0.048 (2)	0.048 (2)	0.041 (2)	0.007 (2)	0.006 (2)	0.011 (2)
P4	0.038 (2)	0.054 (2)	0.050 (2)	0.006 (2)	0.000 (2)	0.007 (2)

spectral properties (vide infra). Perspective views of the cobalt and nickel complex cations are shown in Figure 1. Distances and angles about the metal atom are reported in Table VI. The M–S distances are comparable in the three complexes. Values of distances and angles in the ligand molecule are normal[12] and the dimensions of the anion match those previously reported.[14] There are no intermolecular contacts between nonhydrogen atoms below 3.42 Å.

Complexes I and III exhibit small distortions from the idealized trigonal-bipyramidal geometry, with the metal atom depressed by 0.334 Å (I) and 0.196 Å (III) below the equatorial plane toward the sulfur atom. The chemically equivalent M–P distances in complex III differ from each other more than in complex I. This probably results from a competition between the following factors: the different size of the two metal atoms and the steric requirements of the ligand, on the one hand, and packing forces tending to reproduce the asymmetry of the environment of the complex cation, on the other hand. The geometry of coordination in complex II deviates from the idealized trigonal bipyramidal more than that of the other two complexes. In fact, one of the angles in the equatorial plane (P₁–Co–P₃ = 133.5 (2)°) is considerably larger than the other two (111.8 (2), 112.0 (2)°). A similar distortion toward the square-pyramidal geometry has been found, in varying amounts, for other five-coordinate low-spin Co(II) complexes.[13,15] It has been

Table VI. Bond Lengths (Å) and Angles (deg) within the Coordination Polyhedra (Esd's in Parentheses)

	[Fe(SH)(pp₃)]-BPh₄	[Co(SCH₃)-(np₃)]BPh₄	[Ni(SH)(pp₃)]-BPh₄
	Lengths		
M–S[a]	2.247 (5)	2.186 (5)	2.256 (4)
M–P1	2.346 (6)	2.289 (5)	2.297 (3)
M–P2	2.336 (6)	2.245 (5)	2.292 (4)
M–P3	2.331 (5)	2.270 (5)	2.244 (3)
M–L[b]	2.224 (5)	2.134 (12)	2.157 (3)
	Angles		
S–M–P1	100.5 (2)	88.9 (2)	96.9 (1)
S–M–P2	98.2 (2)	98.8 (2)	95.5 (1)
S–M–P3	96.0 (2)	99.2 (2)	92.5 (1)
S–M–L	177.5 (2)	173.5 (4)	177.3 (3)
P1–M–P2	114.4 (2)	112.0 (2)	114.2 (1)
P1–M–P3	123.0 (2)	133.5 (2)	125.2 (1)
P2–M–P3	116.6 (2)	111.8 (2)	118.5 (1)
L–M–P1	81.6 (2)	84.6 (3)	85.1 (1)
L–M–P2	82.1 (2)	84.3 (3)	85.4 (1)
L–M–P3	81.7 (2)	84.9 (3)	84.8 (1)

[a] M = Fe, Co, or Ni. [b] L = P4 for the iron and nickel complexes; L = N for the cobalt complex.

attributed to the operation of a Jahn–Teller mechanism in the orbitally degenerate ground state of the d⁷ low-spin configuration in D_{3h} or C_{3v} symmetry.[15] The same mechanism should
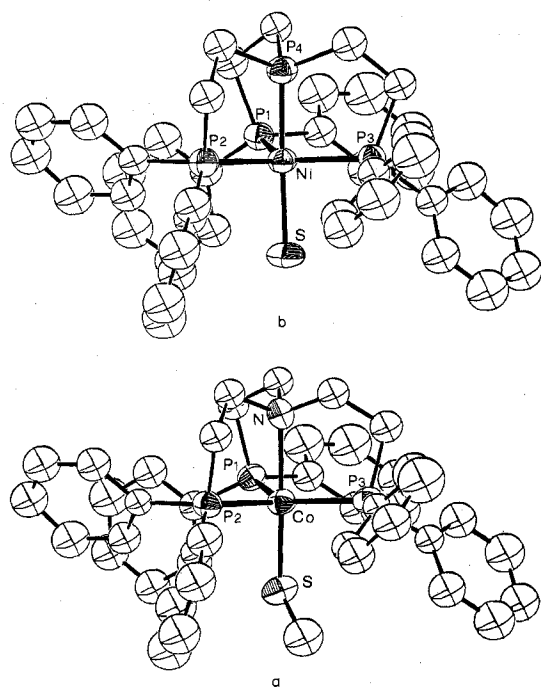
Figure 1. Perspective views of the cations in the structures of (a) [Co(SCH₃)(np₃)]BPh₄ and (b) [Ni(SH)(pp₃)]BPh₄.
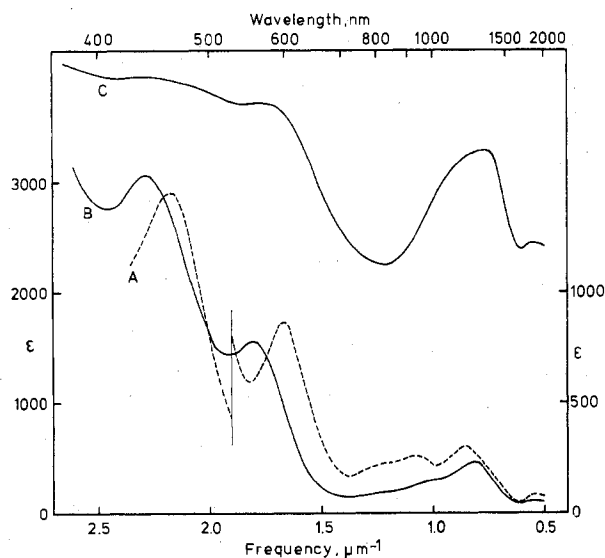
Figure 2. Absorption spectra of [Fe(SCH₃)(pp₃)]BPh₄ (A) and [Fe(SH)(pp₃)]BPh₄ (B) in nitroethane solution. Solid-state spectrum (arbitrary scale) of [Fe(SH)(pp₃)]BPh₄ (C).

Figure 3. Absorption spectra of [Co(SH)(pp₃)]BPh₄ (A) and [Co(SCH₃)(np₃)]BPh₄ (B) in nitroethane solution. Solid-state spectrum (arbitrary scale) of [Co(SCH₃)(np₃)]BPh₄ (C).
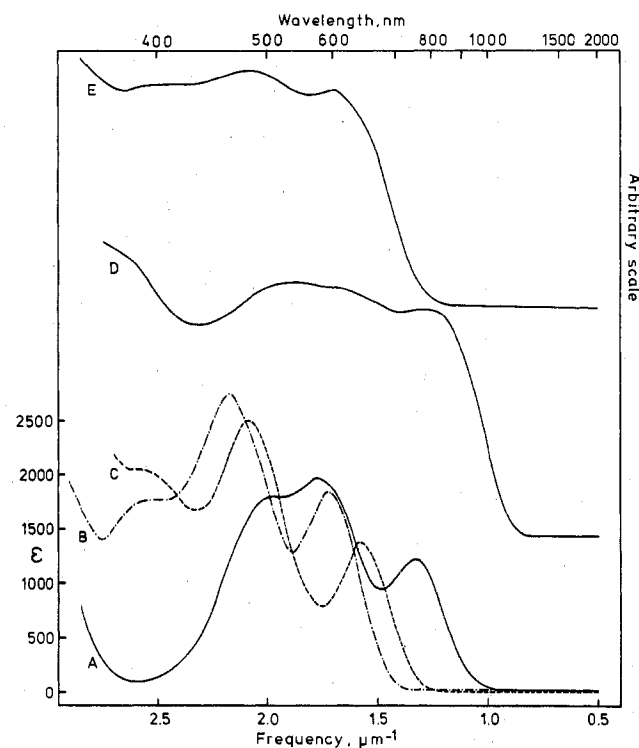
Figure 4. Absorption spectra of [Ni(SH)(np₃)]BPh₄ (A), [Ni-(SH)(pp₃)]BPh₄ (B), and [Ni(SCH₃)(pp₃)]BPh₄ (C) in nitroethane solution. Solid-state spectra (arbitrary scale) of [Ni(SH)(np₃)]BPh₄ (D) and [Ni(SH)(pp₃)]BPh₄ (E).

be invoked in the present case, as the difference in the coordination between complex II and its two isomorphs could hardly be attributed to the small differences in packing between the complexes, considering in particular that the present ligands are quite flexible. Neither can the distortion in complex II be ascribed to the presence of a methyl substituent on the sulfur atom: indeed the projection of the S–C bond on the equatorial plane falls outside the large P₁–Co–P₃ angle. Also, the solvent molecule in the structure of the cobalt compound lies outside the region subtended by that angle.

In the IR spectra of the compounds no bands were observed that could be assigned to the H–S stretching frequencies.

The electronic spectra of the compounds are summarized in Table VII and are shown in Figures 2–4. The reflectance spectra are closely similar to the corresponding absorption spectra in nitroethane. Substitution of H by CH₃ in the –SR group does not produce sensible changes in the spectra. In
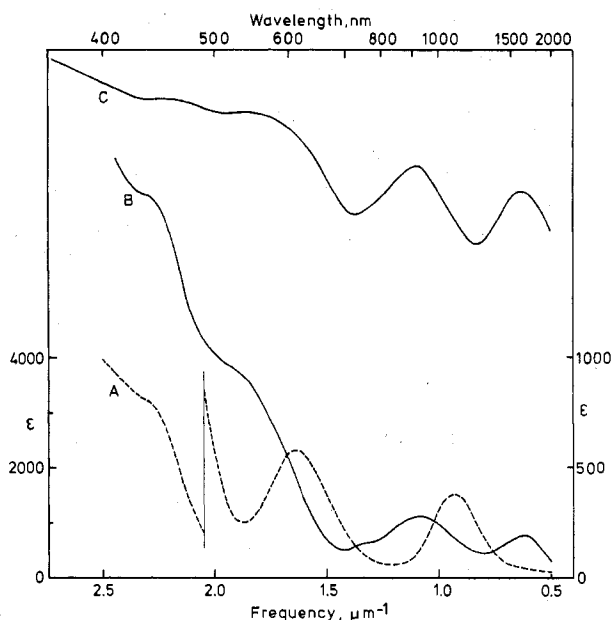
the case of the cobalt complexes, substitution of the np₃ ligand by pp₃ produces some alterations of the general features of the spectra, whereas for the nickel complexes only a blue shift of the bands is observed. The spectra are essentially similar to those previously reported[16,17] for complexes having similar geometry and spin state of the metals; notable differences involving the intensities of the bands in the nickel spectra are discussed below.

In the case of the iron compounds, transitions in the 0.8–1.3-μm^{-1} region may be assigned as $e''^4 e'^2 \rightarrow e''^3 e'^3$ in the

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

Compd	Absorption max,[a] μm^{-1} (ϵ_M for soln)
[Fe(SH)(pp₃)]BPh₄	a: 0.55, 0.78, 0.95 sh, 1.75 sh, 2.30 sh
	b: 0.55 (55), 1.00 sh, 1.80 (780), 2.27 (1540)
[Fe(SCH₃)(pp₃)]BPh₄	a: 0.55, 0.81, 0.95 sh, 1.72, 2.13
	b: 0.55 (80), 0.86 (300), 1.07 (260), 1.23 sh, 1.67 (870), 2.18 (2900)
[Co(SH)(pp₃)]BPh₄	a: 0.93, 1.66
	b: 0.93 (370), 1.63 (570), 2.27 sh
[Co(SCH₃)(pp₃)]BPh₄	a: 0.95, 1.43, 2.10 sh, 2.38 sh
	b: 0.91 (480), 1.47 (540), 1.67 sh
[Co(SH)(np₃)]BPh₄	a: 0.67, 1.19, 1.87 sh, 2.41 sh
	b: 0.69 (94), 1.25 (160), 1.89 sh, 2.40 sh
[Co(SCH₃)(np₃)]BPh₄·(CH₃)₂CO	a: 0.63, 1.10, 1.85 sh, 2.25 sh
	b: 0.63 (190), 1.10 (280), 1.33 sh, 1.90 sh, 2.30 sh
[Ni(SH)(pp₃)]BPh₄	a: 1.70 sh, 2.10, 2.50 sh
	b: 1.72 (1840), 2.17 (2740), 2.55 sh
[Ni(SCH₃)(pp₃)]BPh₄	a: 1.74 sh, 2.04 sh, 2.50 sh
	b: 1.58 (1380), 2.08 (2500), 2.55 sh
[Ni(SH)(np₃)]BPh₄	a: 1.30, 1.68 sh, 1.90 2.65 sh
	b: 1.33 (1230), 1.78 (1980), 1.95 sh
[Ni(SCH₃)(np₃)]BPh₄	a: 1.20, 1.65 sh, 2.00
	b: 1.16, 1.74, 1.89 sh[b]

[a] Key: a, solid; b, nitroethane solution. [b] The compound decomposes in solution.

strong-field limit. D_{3h} symmetry labels are used here, for consistency with previous assignments,[16] although the presence of at least two components in this region of the spectrum is consistent with C_{3v} effective symmetry. The bands at ca. 1.7 and 2.2 μm^{-1} may be respectively assigned as $e''^4 e'^2 \rightarrow e''^4 e' a_1'$ and $e''^4 e'^2 \rightarrow e''^3 e'^2 a_1'$. The two C_{3v} components expected for the latter transition appear to be resolved in the low-temperature spectrum of [Fe(SH)(pp₃)]⁺. The weak band at 0.55 μm^{-1}, that cannot be due to overtones of the ligand, being absent in the spectra of the other pp₃ derivatives, may be attributed to spin-forbidden transitions to the levels originating from the ^5D free-ion term.

The spectra of the np₃ and those of the pp₃ cobalt derivatives are respectively similar to the spectra previously reported for analogous complexes formed with the same ligands.[15c-17] Changes in the spectra due to substitution of the ligand are more significant than those due to distortions of the chromophore. Bands above 1 μm^{-1} should be due to the numerous transitions originating from $e''^4 e'^3 \rightarrow e''^4 e'^2 a_1'$ and $e''^4 e'^3 \rightarrow e''^3 e'^3 a_1'$, and that at ca. 0.9 μm^{-1} (pp₃ derivatives) or 0.6 μm^{-1} (np₃ derivatives) may be assigned to the unique spin-allowed transition arising from $e''^4 e'^3 \rightarrow e''^3 e'^4$. The powder ESR spectrum of [Co(SCH₃)(np₃)]BPh₄ measured with a Varian E-9 apparatus yielded molecular g values of 2.05, 2.14, and 2.23: the absence of considerable anisotropy agrees with the distortion from the trigonal symmetry in the coordination.

The spectra of the nickel derivatives of this series exhibit an unusual feature. In fact, *two* intense bands are recorded in the region above 1.5 μm^{-1}, whereas only one intense band is generally observed ($e''^4 e'^4 \rightarrow e''^4 e'^3 a_1'$).[17] A second, much weaker band that is often observed at higher energies is assigned to the symmetry-forbidden transition $e''^4 e'^4 \rightarrow e''^3 e'^4 a_1$.[17] Both are allowed in C_{3v} symmetry, but their relative intensities indicate that D_{3h} effective symmetry is generally operative. Breakdown of the D_{3h} selection rules in the present complexes should be attributed to the presence of the sulfur ligand, whose orbitals are probably thoroughly involved in formation of the "antibonding d levels". Assignment of the two bands as components of the low-energy transition, split by a spin–orbit or Jahn–Teller mechanism in the excited state,[18] may be ruled out in view of their large separation (ca. 0.5 μm^{-1}).

It should be observed that the iron complexes of this series possess a triplet ground state, whereas those of ref 19 present a singlet–triplet equilibrium, in spite of the fact that the $\sum n°$ values[20] for the two donor sets involved (P₄S and P₄X) are comparable. The difference is probably due to the different geometry of five-coordination and to the fact that the mean

of the Fe–P distances is larger (by 0.07 Å) in the present compounds.

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Supplementary Material Available: Tables of bond distances and structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

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