Crystal and Molecular Structure of Tetramethyldithioimidodiphosphinic Acid, $(SPMe_2)_2NH$, and Its Cobalt(II) Complex, $Co[(SPMe_2)_2N]_2$, Containing a Tetrahedral CoS_4 Core

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Introduction

The interest in metal complexes of tetraorganodithioimidodiphosphinato ligands, $[R_2P(S)NP(S)R'_2]^-$ (R, R′ = alkyl, aryl), is mainly due to the unusual flexibility of the SPNPS system. This allows the formation of chelate rings in which the ligand usually exhibits a symmetrical coordination pattern through both sulfur atoms.[2,3] The larger S···S "bite" (ca 4 Å) of this type of chelating thiophosphorus ligands, compared to 1,1-dithiolato ligands (ca. 3 Å), produces less strain in the ring and permits a different coordination geometry around the metal atom. Therefore comparative studies with 1,1-dithiophosphorus ligands, $S_2PR_2^-$ (R = alkyl, aryl, alkoxy, aryloxy) are of certain interest. For example, all $Ni(S_2PR_2)_2$ (R = Me,[4] Et,[5] Ph,[6] OMe,[7] OEt[8]) compounds investigated so far exhibit a square-planar NiS_4 system, while for $Ni[(SPMe_2)_2N]_2$ a structure containing a tetrahedral NiS_4 core has been established.[9,10]

Several studies on metal tetraphenyldithioimidodiphosphinates, $M[(SPPh_2)_2N]_n$, were reported.[2,3] In contrast, the methyl analogues, $M[(SPMe_2)_2N]_n$, were less investigated (only inorganic derivatives of Pb(II),[11] Bi(III),[12] Fe(II),[13−15] Co(II),[14,16−18] Ni(II),[9,10,14] Pd(II), Pt(II), and Zn(II)[14] are known), due, perhaps, to the tedious synthesis of the free ligand. Only the molecular structure of iron(II) and nickel(II) complexes has been investigated by X-ray diffraction, both compounds containing a tetrahedral MS_4 core. In contrast, the related cobalt(II) and nickel(II) dithioacetylacetonates, $M[(SCMe)_2CH]_2$, exhibit a molecular structure based upon square-planar MS_4 coordination geometry.[19]

Here we wish to report the crystal and molecular structure of the free ligand, $(SPMe_2)_2NH$, and of its cobalt(II) complex, which, to the best of our knowledge, is the first cobalt(II) derivative containing only dithiophosphorus anionic ligands characterized by X-ray diffractometry.

Experimental Section

Preparation of $(SPMe_2)_2NH$. The free ligand was prepared from $Me_2P(S)NH_2$ and $Me_2P(S)Br$, in presence of $KOBu^t$, using a published procedure.[20] Colorless prisms were obtained after recrystallization from water, and suitable crystals for X-ray diffractometry were grown from a $CHCl_3$/n-hexane mixture. Mp: 177−180 °C (lit.:[20] 178 °C). IR (KBr): $\nu_{as}(P_2NH)$ 910 vs, $\nu(PC)$ 760 ms, 740 m, $\nu(PS)$ 584 s, 565 w,sh cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.04 m ($^2J(PCH) + {}^4J(PNPCH) = 12.9$ Hz) (CH_3); 4.37 s (N*H*). ^{13}C NMR ($CDCl_3$): δ 26.3 m ($^1J(PC) + {}^3J(PNPC) = 66.9$ Hz). ^{31}P NMR ($CDCl_3$): δ 60.4 s.

Preparation of $K[(SPMe_2)_2N]$. Stoichiometric amounts of $(SPMe_2)_2NH$ (10.05 g, 0.05 mol) and $KOBu^t$ (5.6 g, 0.05 mol) in 200 mL of anhydrous benzene were stirred under reflux for 36 h. The insoluble solid product was filtered, washed several times with benzene, and dried *in vacuo*. Yield 11.5 g (96%). Mp: 235−237 °C. IR (KBr): $\nu_{as}(P_2N)$ 1150 vs, br, $\nu(PC)$ 750 m, 730 s, 715 s, 665 ms, $\nu(PS)$ 567 vs, 545 ms cm^{-1}. ^1H NMR (CD_3OD): δ 1.80 m ($^2J(PCH) + {}^4J(PNPCH) = 12.1$ Hz). ^{13}C NMR (CD_3OD): δ 28.37 m ($^1J(PC) + {}^3J(PNPC) = 77.3$ Hz). ^{31}P NMR (CD_3OD): δ 44.0 s.

Preparation of $Co[(SPMe_2)_2N]_2$. Clear methanolic solutions containing $CoCl_2 \cdot 6H_2O$ (0.198 g, 0.83 mmol, in 15 mL of MeOH) and $K[(SPMe_2)_2N]$ (0.4 g, 1.67 mmol, in 15 mL of MeOH) were mixed and stirred for 1 h, at room temperature. The reaction mixture was filtered, and the clear blue solution was concentrated, resulting in precipitation of a blue-green crystalline product. Recrystallization from CH_2Cl_2/n-hexane gave 0.29 g (75%) of $Co[(SPMe_2)_2N]_2$, as dark blue-green prisms. Mp: 202−204 °C (lit.:[14] 202−204 °C). IR (KBr): $\nu_{as}(P_2N)$ 1190 vs, $\nu(PC)$ 744 m, 710 m, 675 vs, $\nu(PS)$ 520 m, 500 s, $\nu(CoS)$ 375 m, 330 m, 310 ms cm^{-1}. ^1H NMR ($CDCl_3$): δ −2.44 s, br. ^{31}P NMR ($CDCl_3$): δ −2.7 s.

Crystallography. Data for both crystals were collected at room temperature (293 K) on a Siemens P4 four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), using the $\omega/2\theta$ scan mode. Intensities were corrected for Lorentz−polarization, but not for absorption. The structures were solved by direct methods and were refined by full-matrix least-squares methods using the SHELXTL PLUS (PC) program system.[21] Details of the crystal data, measurement of intensities, and data processing are summarized in Table 1. All non-hydrogen atoms were refined anisotropically. For $(SPMe_2)_2NH$ the N−*H* atom was located from a difference map. The positions of the other hydrogen atoms in both structures were calculated as a riding model, with fixed, isotropic temperature factor $U = 0.06$ Å^2.

Results and Discussion

The spectral characteristics of the free $(SPMe_2)_2NH$ acid (IR, NMR) and of its cobalt complex (IR) have been described and extensively discussed in previous publications,[14,16−18,20] and need no further comment. The samples investigated in this work displayed properties identical to those previously reported. It should be noted that the paramagnetic behavior (both in solid state and CH_2Cl_2 solution) and the electronic spectrum of $Co[(SPMe_2)_2N]_2$ complex are consistent with a tetrahedral coordination geometry.[14]

The ^1H NMR spectrum of the cobalt complex shows only one broad resonance at −2.4 ppm, this behavior being due to its paramagnetic character. At room temperature, only one ^{31}P resonance (shifted about 60 ppm to higher field relative to the

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Table 1. Crystallographic Data for $(SPMe_2)_2NH$ and $Co[(SPMe_2)_2N]_2$

	$(SPMe_2)_2NH$	$Co[(SPMe_2)_2N]_2$
chem formula	$C_4H_{13}NP_2S_2$	$C_8H_{24}CoN_2P_4S_4$
cryst size (mm)	0.4 × 0.36 × 0.2	0.24 × 0.24 × 0.28
	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a (Å)	8.245(4)	15.382(6)
b (Å)	11.615(4)	8.849(2)
c (Å)	20.987(6)	16.092(5)
β (deg)		106.24(2)
V (Å^3)	2009.7(14)	2102.9(15)
Z	8	4
D_{calcd} (g cm^{-3})	1.330	1.451
μ(Mo Kα) (mm^{-1})	0.779	1.507
weighing scheme	$[\sigma^2(F) + 0.0001F^2]^{-1}$	$[\sigma^2(F) + 0.0008F^2]^{-1}$
R^a (%)	4.36	4.94
$R_w{}^a$ (%)	3.76	4.72
residual $\Delta\varrho$: max, min (e Å^{-3})	0.32, −0.26	0.39, −0.49

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$; $R_w = [\Sigma(w\Delta)^2/\Sigma wF_o2]^{1/2}$; $\Sigma = [\Sigma w\Delta^2/(NO - NV)]^{1/2}$; $\Delta = F_o - F_c$.

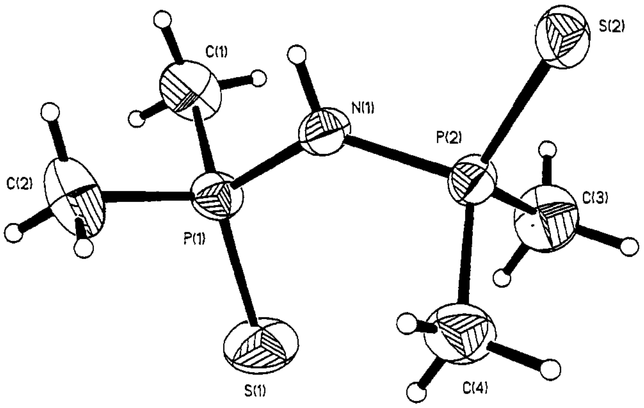

Figure 1. Molecular structure of the monomeric unit $(SPMe_2)_2NH$.

Table 2. Interatomic Distances (Å) and Angles (deg) in $(SPMe_2)_2NH$

P(1)−N(1)	1.679(3)	P(2)−N(1)	1.675(3)
P(1)−S(1)	1.939(2)	P(2)−S(2)	1.962(2)
N(1)−H(1′)	0.894(5)	S(2a)···H(1′)	2.513(5)
S(1)−P(1)−N(1)	114.0(1)	S(2)−P(2)−N(1)	107.9(1)
S(1)−P(1)−C(1)	114.2(2)	S(2)−P(2)−C(3)	113.7(2)
S(1)−P(1)−C(2)	114.0(2)	S(2)−P(2)−C(4)	113.3(2)
N(1)−P(1)−C(1)	103.8(2)	N(1)−P(2)−C(3)	108.0(2)
N(1)−P(1)−C(2)	104.98(2)	N(1)−P(2)−C(4)	108.1(2)
C(1)−P(1)−C(2)	104.9(2)	C(3)−P(2)−C(4)	105.5(2)
P(1)−N(1)−P(2)	133.2(2)		
P(1)−N(1)−H(1′)	107.8(4)	N(1)−H(1′)···S(2a)	175.9(4)
P(2)−N(1)−H(1′)	119.0(4)		

Table 3. Interatomic Distances (Å) and Angles (deg) in $Co[(SPMe_2)_2N]_2$

Co−S(1)	2.310(2)	Co−S(3)	2.307(3)
Co−S(2)	2.317(2)	Co−S(4)	2.323(2)
P(1)−S(1)	2.021(2)	P(3)−S(3)	2.012(3)
P(1)−N(1)	1.588(5)	P(3)−N(2)	1.598(6)
P(2)−N(1)	1.585(5)	P(4)−N(2)	1.584(6)
P(2)−S(2)	2.029(2)	P(4)−S(4)	2.023(2)
Co−S(1)−P(1)	103.2(1)	Co−S(3)−P(3)	102.4(1)
S(1)−P(1)−N(1)	116.5(2)	S(3)−P(3)−N(2)	117.3(2)
P(1)−N(1)−P(2)	128.0(3)	P(3)−N(3)−P(4)	130.3(3)
S(2)−P(2)−N(1)	117.2(2)	S(4)−P(4)−N(2)	116.9(2)
Co−S(2)−P(2)	101.8(1)	Co−S(4)−P(4)	100.8(1)
S(1)−Co−S(2)	109.6(1)	S(3)−Co−S(4)	110.3(1)
S(1)−Co−S(3)	114.3(1)	S(2)−Co−S(4)	111.7(1)
S(1)−Co−S(4)	108.0(1)	S(2)−Co−S(3)	103.0(1)

free acid) was observed, suggesting equivalence of phosphorus atoms in the molecule.

Like the phenyl analogue, $(SPPh_2)_2NH$,[22-24] the molecule of $(SPMe_2)_2NH$ displays an *anti* conformation of the sulfur atoms (Figure 1), with a dihedral angle between S(1)P(1)N(1) and N(1)P(2)S(2) planes of 176.9°; the PNP system is bent (P(1)−N(1)−P(2) 133.2(2)°). However, important differences should be noted in the crystal. The lattice of $(SPPh_2)_2NH$ contains discrete dimeric associations through N−H···S(2a) hydrogen bonds.[23] By contrast, in the crystal of $(SPMe_2)_2NH$ (Figure 2) the molecules are associated into polymeric chains through N(1)−H(1′)···S(2a) bonds. Since only one of the P=S bonds participates in hydrogen bonding, differences between the phosphorus−sulfur bond distances in the monomeric unit are observed (Table 2), the double P=S bond involved in the hydrogen bonding being longer. However, in the S_2P_2N system the phosphorus−nitrogen bonds are equal (average 1.677 Å) and of the same magnitude as the single P−N bond (1.662(2) Å) in $[(Me_3Si)_2N{-}P({=}NBu^t)S]_2$.[25]

The crystal of the cobalt complex contains discrete $Co[(SPMe_2)_2N]_2$ molecules (Figure 3), in which both imidodiphosphinato ligands act as isobidentate moieties (average Co−S 2.314 Å) (Table 3). The closest intermolecular contact is 2.70 Å, between nitrogen and hydrogen atoms of neighboring molecules. The compound can be described as a *spiro*-bicyclic structure, with cobalt as the spiro atom. To allow chelate ring closure the SPNPS fragment changes its conformation, bringing the sulfur atoms in a *syn* orientation with respect to the PNP system. As a consequence, the dihedral angles S(1)P(1)N(1)/S(2)P(2)N(1) (119.1°) and S(3)P(3)N(2)/S(4)P(4)N(2) (124.2°) are diminished in comparison with that observed in the free acid (176.9°). The slightly distorted tetrahedral arrangement of sulfur atoms around the metal is reflected in the magnitude of the S−Co−S angles (range 103.0−114.3°) and the dihedral angle between CoS(1)S(2) and CoS(3)S(4) planes (84.6°). The structural parameters of the CoS_4 core in $Co[(SPMe_2)_2N]_2$ compare very well to those of the cation in the blue isomer of the $[Co(Me_3AsS)_4][ClO_4]_2$ (average Co−S 2.30 Å, S−Co−S range 102.0−120.4°, CoS(1)S(2)/CoS(3)S(4) dihedral angle 86.4°).[26]

The six-membered CoS_2P_2N inorganic rings contain equal P−S (average 2.021 Å) and P−N (average 1.589 Å) bonds, of intermediate magnitude between single P−S and double P=S bonds (cf. 2.139(1) and 1.930(1) Å in $Ph_2P({=}S){-}S{-}S{-}P({=}S)$-$Ph_2$,[27] or 2.069(3) and 1.956(3) Å in $Ph_2P({=}S){-}N{=}P({-}SMe)$-$Ph_2$,[28]), and single P−N and double P=N bonds (cf. 1.662(2) and 1.529(2) Å in $[(Me_3Si)_2N{-}P({=}NBu^t)S]_2$,[25] or 1.610(4) and 1.568(4) Å in $Ph_2P({=}S){-}N{=}P({-}SMe)Ph_2$,[28]), respectively. Similar values (*ca.* 1.58 Å) were reported for the $P\underline{\cdots}N$ bond lengths in phosphazene trimers, $P_3N_3X_3$.[29] Compared to the free acid, while the phosphorus−sulfur bonds are lengthened, the phosphorus−nitrogen bonds are strengthened, being con-

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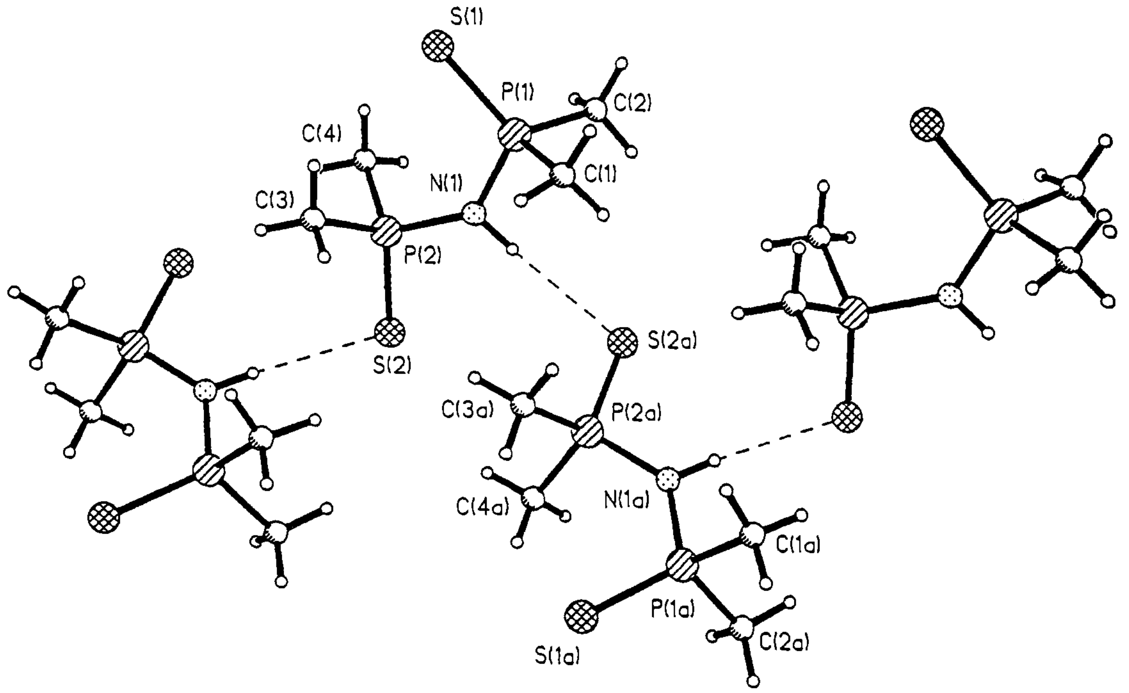

Figure 2. View of the polymeric association through N–H···S bonds in the crystal of $(SPMe_2)_2NH$.

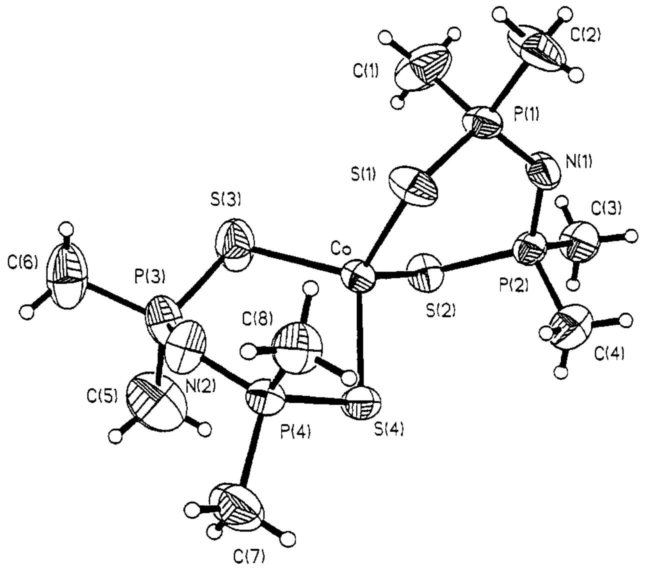

Figure 3. Molecular structure of the monomeric $Co[(SPMe_2)_2N]_2$.

sistent with a considerable double bond character of both bond types. The difference in the S–P–N angles, observed in the molecule of the free acid has disappeared in the chelate rings (average 117°), and the P–N–P angles (average 129.2°) are slightly diminished with respect to the free acid (P–N–P 133.2°). Despite this averaging in bond lengths and angles, suggesting that at least some delocalization of π-electrons over the SPNPS fragment occurs by chelate formation, the CoS_2P_2N rings are not planar. They exhibit a twisted boat conformation, with P(1), S(2) and P(3), S(4) atoms on opposite sides with respect to the best CoS(1)P(2)N(1) and CoS(3)P(4)N(2) planes, respectively.

In the $M[(SPMe_2)_2N]_2$ (M = Fe, Co, Ni) series the Ni and Co complexes are isomorphous, but different from the Fe analog.[9,15]

With respect to cobalt(II)–thioligand complexes, it has been observed that $Co(S_2PR_2)_2$ (where R = alkyl, aryl, alkoxy) containing 1,1-dithiophosphorus ligands easily undergo oxidative processes, leading to cobalt(III) derivatives. Amines and phosphines were used to stabilize $Co(S_2PR_2)_2$ complexes toward metal oxidation, the adducts thus formed displaying trigonal bipyramidal or octahedral geometries.[30] By contrast, $Co[(SPMe_2)_2N]_2$ is stable to oxidation both in solution and solid state, thus providing the first example of monomeric Co(II) complex of a thiophosphorus ligand containing a tetrahedral CoS_4 core.

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Supplementary Material Available: Tables giving crystal data, data collection, parameters, and solution and refinement data, bond lengths, bond angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for each structure and a drawing showing the unit cell of $(SPMe_2)_2NH$ (9 pages). Ordering information is given on any current masthead page.

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