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Bis(thiophosphinoyl)amines and their neutral cobalt(II) complexes, containing stable tetrahedral CoS_4 cores. Crystal structures of $NH(SPMe_2)(SPPh_2)$ and $[Co\{(SPMe_2)(SPPh_2)N\}_2]$

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The compound $NH(SPMe_2)(SPPh_2)$ was prepared using a new method, *i.e.* the reaction between $Li[HN(S)PPh_2]$ and $Me_2P(S)Cl$ in a diethyl ether–*n*-hexane mixture. The complex $[Co\{(SPMe_2)(SPPh_2)N\}_2]$ was obtained by the reaction of $CoCl_2\cdot6H_2O$ and $K[(SPMe_2)(SPPh_2)N]$ in methanol. The crystal and molecular structure of both the free acid $NH(SPMe_2)(SPPh_2)$ and its cobalt(II) complex $[Co\{(SPMe_2)(SPPh_2)_2N\}_2]$ were determined using X-ray diffractometry. The acid exhibits an *anti* conformation of the sulfur atoms in the SPNPS system and dimeric pairs are formed in the crystal through N(1)–H(1) · · · S(2a) [2.43(9) Å] hydrogen bonds, which involve only the sulfur atom of the S=PPh$_2$ group of each molecule. The cobalt complex consists of discrete, monomeric molecules, with isobidentate ligands [average Co–S 2.32(1), average P–S 2.031(5) Å] and a distorted tetrahedral CoS_4 core (S–Co–S range 102.7–117.7°). The structures of both the free acid and its cobalt(II) derivative are discussed in relation with other bis(thiophosphinoyl)amines and metal complexes containing a CoS_4 core.

Neutral cobalt(II) complexes containing 1,1-dithio ligands (dithiocarbamates, dithiophosphinates, dithiophosphates) are unstable being readily oxidized to the corresponding cobalt(III) derivatives. Dithiophosph(in)ato $Co(S_2PR_2)_2$ complexes (where R = alkyl, aryl or alkoxy) can be stabilized towards metal oxidation, by forming square-pyramidal or octahedral adducts with amines and phosphines.[1] The stability of dithiocarbamato derivatives, $Co(S_2CNR_2)_2$, improves with the use of larger peripheral alkyl R groups and in some cases a square planar–tetrahedral equilibrium was suggested.[2] However, no X-ray diffractometry investigation was performed for such complexes. To our knowledge, so far the molecular structures of only two monomeric, neutral cobalt(II) complexes containing dithio ligands have been reported, *i.e.* bis(dithioacetylacetonato)-cobalt(II), $[Co\{(SCMe)_2CH\}_2]$[3] and $[Co\{(SPMe_2)_2N\}_2]$,[4] which exhibit square-planar and tetrahedral CoS_4 cores, respectively.

Usually the bis(thiophosphinoyl)amide anions $[N(SPR_2)(SPR'_2)]^-$ (R, R′ = alkyl or aryl) are symmetrically co-ordinated through both sulfur atoms.[5–7] The interest in metal complexes containing this type of ligand is mainly due to the unusual flexibility of the SPNPS system and the large S · · · S 'bite' (*ca.* 4 Å) which allows the ligand moiety to accommodate the requirements of various metal co-ordination geometries. For example, $[Ni\{(SPR_2)(SPR'_2)N\}_2]$ complexes, containing symmetric ligands (R = R′ = Me[8,9] or Ph[10,11]), exhibit a tetrahedral NiS_4 core. By contrast the nickel(II) complex of the related asymmetric ligand, $[Ni\{(SPMe_2)(SPPh_2)N\}_2]$, shows a molecular structure based upon square-planar NiS_4 co-ordination geometry.[10] On the other hand, changes in the organic groups attached to phosphorus atoms result in differences in the crystal structure of the free bis(thiophosphinoyl)amine, *i.e.* dimer and chain polymer associations through N–H · · · S were observed for the symmetric $NH(SPPh_2)_2$[12] and $NH(SPMe_2)_2$[4] derivatives.

Here we report the crystal and molecular structure of the free asymmetric amine $NH(SPMe_2)(SPPh_2)$ and of its cobalt(II) complex, which are discussed in relation to other bis(thiophosphinoyl)amines and cobalt(II) complexes containing CoS_4 cores.

Experimental

Materials and instrumentation

Infrared spectra were run in the range 4000–200 cm^{-1} on a Perkin-Elmer 283B spectrometer, as KBr discs, electronic spectra in $CHCl_3$ solution on a Shimadzu UV160U spectrophotometer and ^1H, ^{13}C and ^{31}P NMR spectra on a Varian GEMINI 300 instrument operating at 299.5, 75.4 and 121.4 MHz, respectively. The chemical shifts (δ) in ppm are relative to $SiMe_4$ or 85% H_3PO_4, respectively. Positive-ion fast atom bombardment, FAB(+), and 70 eV (*ca.* 1.12×10^{-17} J) electron impact (EI) mass spectra were recorded using JEOL SX-102A and Hewlett-Packard MS-598 instruments, respectively.

Preparations

$NH(SPMe_2)(SPPh_2)$. A solution of LiBu^n in *n*-hexane (40.3 cm^3, 1.565 M, 63.1 mmol) was added dropwise to a stirred suspension of $Ph_2P(S)NH_2$ (15.03 g, 64.5 mmol) in anhydrous diethyl ether (150 cm^3), under an argon atmosphere. The reaction mixture was cooled to room temperature, and then a solution of $Me_2P(S)Cl$ (5.58 g, 32.25 mmol) in anhydrous diethyl ether (50 cm^3) was added dropwise. About 100 cm^3 of the solvent was distilled off, water (150 cm^3) was added to the resulting suspension, and the remaining organic solvent was removed under vacuum. The viscous solution thus obtained was filtered and from the solid product $Ph_2P(S)NH_2$ was recovered (7.4 g, after recrystallization from toluene). The clear viscous filtrate containing the lithium salt of the required compound was treated with 10% HCl until no more solid product deposited. The white solid product was collected by suction filtration and recrystallized from ethanol as colourless crystals. Yield: 9.27 g (89%), m.p. 157–159 °C (lit.,[13] 156–157 °C) (Found: C, 51.53; H, 5.38; N, 4.25. $C_{14}H_{17}NP_2S_2$ requires C, 51.67; H, 5.27; N, 4.30%); IR (cm^{-1}) ν(NH) 2550s, $\nu_{asym}(P_2NH)$ 905vs, ν(PC) 740s, 720s, 710s, 685s, ν(PhPS) 620s, ν(MePS) 585m; $\delta_H(CDCl_3)$ 2.07 [6 H, d, ^2J(PH) 13.6, CH_3], 4.28 [1 H, s(br), NH], 7.50 (6 H, m, *m*- and *p*-H of Ph) and 7.86 [4 H, ddd, ^3J(PH) 14.3, ^3J(HH) 8.0, ^4J(HH) 1.6 Hz, *o*-H of Ph]; δ_C($CDCl_3$) 25.13 [d, ^1J(PC) 66.1, CH_3], 128.75 [d, ^3J(PC) 13.2, C_m], 131.00 [d, ^2J(PC) 11.6, C_o], 132.25 [d, ^4J(PC) 3.2, C_p] and 134.48 [d, ^1J(PC) 101.2 Hz, C_{ipso}]; δ_P($CDCl_3$): 51.3 [d, ^2J(PP) 22.8, PhPS] and 63.9 [d, ^2J(PP) 22.8 Hz, MePS]; EI mass spectrum *m*/*z* 325 (100, M^+), 292 (58, $Me_2Ph_2P_2SN^+$), 217 (50, Ph_2PS^+), 216 (72, $Me_2PhP_2SNH^+$), 183 (32, Me_2PNPPh^+), 139 (49, $Me_2P_2SNH^+$), 122 (29, $PhPN^+$), 107 (16, Me_2PSN^+) and 93 (32%, Me_2PS^+).

K[($SPMe_2$)($SPPh_2$)N]. This compound was prepared as described earlier,[10] from the free acid and KOBu^t in refluxing benzene, m.p. = 251–253 °C. For IR and NMR (^{1}H, ^{13}C, ^{31}P) data see ref. 10.

[Co{($SPMe_2$)($SPPh_2$)N}$_2$]. Clear methanolic solutions containing $CoCl_2\cdot6H_2O$ (0.013 g, 0.055 mmol, in 15 cm^3 MeOH) and K[($SPMe_2$)($SPPh_2$)N] (0.04 g, 0.11 mmol, in 15 cm^3 MeOH) were mixed and the mixture changed immediately from pink to deep blue. It was stirred for 2 h at room temperature. The blue solid which deposited was then filtered off and recrystallized from benzene to give [Co{($SPMe_2$)($SPPh_2$)N}$_2$] as blue crystals (0.03 g, 77%), m.p. 172–173 °C (Found: C, 47.17; H, 4.66; N, 3.73. $C_{28}H_{32}CoN_2P_4S_4$ requires C, 47.53; H, 4.56; N, 3.96%); IR (cm^{-1}) ν_{asym}(P_2N) 1195vs (br), ν(PC) 750m, 710m, 690vs, ν(PhPS) 565s, ν(MePS) 520s, ν(CoS) 380w, 340mw, 330m; electronic ($CHCl_3$, cm^{-1}) 15 974, 14 184 and 13 193 (sh); FAB (+) mass spectrum *m*/*z* 708 (83, $M + H^+$), 707 (60, M^+), 383 {100, Co[($SPMe_2$)($SPPh_2$)N]$^+$}, 324 [16, ($SPMe_2$)($SPPh_2$)N$^+$], 292 (20, $Me_2Ph_2P_2SN^+$), 260 (4, $Me_2Ph_2P_2N^+$), 217 (9, Ph_2PS^+), 154 (97, Ph_2^+), 138 (49, $Me_2P_2SN^+$), 137 (52, $MePhPN^+$), 107 (17, Me_2PSN^+), 93 (3, Me_2PS^+) and 77 (15%, Ph^+).

Crystallography

A colourless block crystal of NH($SPMe_2$)($SPPh_2$) and a blue block crystal of [Co{($SPMe_2$)($SPPh_2$)N}$_2$], which had been grown from $CHCl_3$–*n*-hexane mixtures, were mounted on glass fibres and sealed with epoxy glue. Data were collected at room temperature on a Rigaku AFC5R diffractomer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), operating at 50 kV and 35 mA, using the ω–2θ scan technique. Cell constants and an orientation matrix for data collection, obtained from 24 carefully centred reflections, corresponded to monoclinic cells of dimensions given in Table 1. On the basis of statistical analyses of intensity distributions and the successful solution and refinement of the structure, the space groups were determined to be *C*2/*c* (no. 15) and *P*2$_1$/*c* (no. 14) respectively (Table 1).

Of the 3262 reflections for compound NH($SPMe_2$)($SPPh_2$) and 6374 for [Co{($SPMe_2$)($SPPh_2$)N}$_2$] which were collected, 3185 and 6130 were unique. The intensities of three representative reflections measured after every 150 remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). Empirical absorption corrections based on azimuthal scans of several reflections were applied which resulted in transmission factors ranging from 0.67 to 1.00 and 0.66 to 1.00. The data were corrected for Lorentz-polarization effects.

The structures were solved by direct methods.[14] For both molecules, all of the non-hydrogen atoms were treated anisotropically with the exception of the carbon atoms of the phenyl rings in the cobalt complex. The hydrogen atom attached to nitrogen was found from the difference map while all other hydrogen atoms were included in their idealized positions with C–H set at 0.95 Å and with isotropic thermal parameters 1.2 times that of the carbon atom to which they were attached.

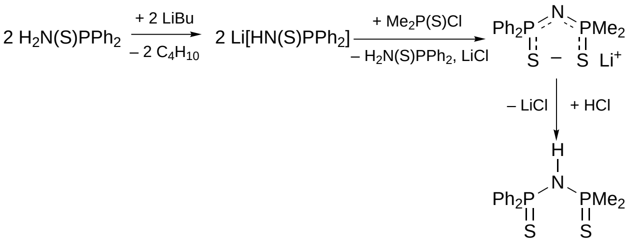
The final cycle of full-matrix least-squares refinement was based on 1252 and 2161 observed reflections [$I > 3.00\sigma(I)$] and 175 and 232 (for **2**) variable parameters and converged (largest parameter shift was 0.001 times its estimated standard deviation) with unweighted and weighted agreement factors of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.0599 and 0.0659 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ = 0.0593 and 0.0599. The standard deviations of an observation of unit weight were 1.66 and 1.54. The weighting scheme was based on counting statistics and included a factor (*p* = 0.004 and 0.015) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, (sin θ)/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.51 and −0.48, and 0.55 and −0.56 e Å^{-3}. All calculations were performed using the TEXSAN[15] crystallographic software package.

CCDC reference number 186/762. Structure-factor tables are available from the authors.

Table 1 Crystallographic data

	NH($SPMe_2$)-($SPPh_2$)	[Co{($SPMe_2$)-($SPPh_2$)N}$_2$]
Molecular formula	$C_{14}H_{17}NP_2S_2$	$C_{28}H_{32}CoN_2P_4S_4$
M	325.36	707.34
Space group	*C*2/*c*	*P*2$_1$/*c*
a/Å	26.582(9)	15.09(1)
b/Å	9.11(1)	11.95(1)
c/Å	16.18(2)	19.132(6)
β/°	120.42(4)	106.75(3)
U/Å^3	3379(6)	3301(4)
Z	8	4
D_c/g cm^{-3}	1.28	1.42
μ(Mo-Kα)/cm^{-1}	4.91	9.74
F(000)	1360.0	1460.0
$2\theta_{max}$/°	50	50
Reflections measured	3262	6374
Reflections observed [$F_o^2 \geqslant 3\sigma(F_o)^2$], N_o	1252	2161
Parameters refined, N_p	175	232
R	0.0599	0.0659
R′ [a]	0.0593	0.0599
Goodness of fit, *S* [b]	1.66	1.54

[a] $w = 1/\sigma^2(F_o)$. [b] $[\Sigma(|F_o| - |F_c|)/\sigma]/(N_o - N_p)$.



Scheme 1

Results and Discussion

The synthesis of NH($SPMe_2$)($SPPh_2$) was previously reported by Schimdpeter and Ebeling[13] based on the reaction of $Ph_2P(S)NH_2$ with $Me_2P(S)Cl$, in the presence of KOBu^t. We prepared the same compound using a new procedure (Scheme 1), *i.e.* the reaction of the lithiated amide Li[HN(S)PPh_2] with $Me_2P(S)Cl$, in a diethyl ether–*n*-hexane mixture. Since LiBu is soluble in diethyl ether, its use instead of KOBu^t[13] allows a better contact between the reactants and improves the yield considerably. This method is also very versatile since various phosphorus amides and chlorides might be used in the coupling reaction. A series of compounds of the type NH(XPR_2)-(YPR'_2) (X = O or S, R, R′ = Me or Ph) has been prepared in our laboratory and work is in progress to prepare similar derivatives containing selenium as a second chalcogen atom.

The IR and ^{31}P NMR spectra of NH($SPMe_2$)($SPPh_2$) have previously been described and discussed in comparison with

Table 2 Important bond lengths (Å) and angles (°) for $NH(SPMe_2)(SPPh_2)$*

N–P(1)	1.698(7)	P(2)–C(3)	1.80(1)
N–P(2)	1.692(6)	P(2)–C(9)	1.791(9)
P(1)–S(1)	1.962(3)		
P(1)–C(1)	1.78(1)	N–H(1)	1.01(8)
P(1)–C(2)	1.793(9)	H(1)···S(1′)	2.43(9)
P(2)–S(2)	1.946(3)	N···S(1′)	3.371(7)
N–P(1)–S(1)	109.6(3)	N–P(2)–C(9)	106.0(4)
N–P(1)–C(1)	106.8(4)	S(2)–P(2)–C(3)	112.5(3)
N–P(1)–C(2)	108.1(4)	S(2)–P(2)–C(9)	114.1(3)
S(1)–P(1)–C(1)	112.4(3)	C(3)–P(2)–C(9)	107.2(4)
S(1)–P(1)–C(2)	113.8(3)	P(1)–N–P(2)	126.1(4)
C(1)–P(1)–C(2)	105.8(5)	P(1)–N–H(1)	114(5)
N–P(2)–S(2)	113.4(3)	P(2)–N–H(1)	119(5)
N–P(2)–C(3)	102.7(4)	N–H(1)···S(1′)	156(6)

* Symmetry-equivalent positions $-x$, $1-y$, $1-z$ are denoted by primes.

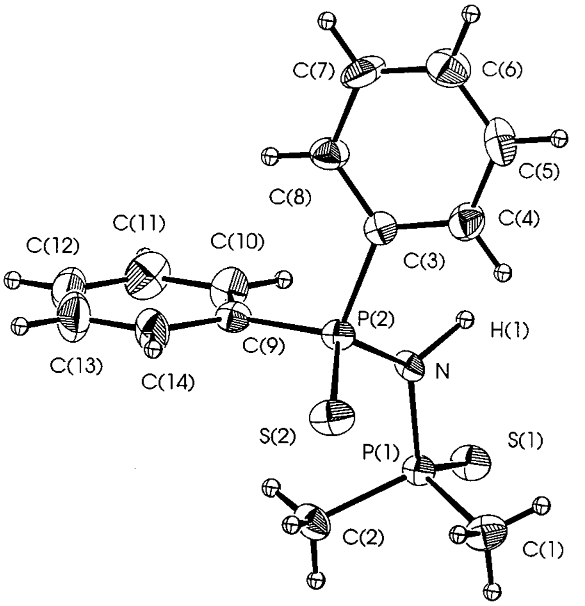


Fig. 1 An ORTEP-like drawing of the monomeric unit of $NH(SPMe_2)(SPPh_2)$

Table 3 Comparative structural data (bond lengths in Å, angles in °) for bis(thiophosphinoyl)amines

	$NH(SPR_2)(SPR'_2)$		
	R = R′ = Ph (ref. 12)	R = Me, R′ = Ph (this work)	R = R′ = Me (ref. 4)
P(1)–S(1)	1.950(1)	1.962(3)[a]	1.962(2)
P(2)–S(2)	1.937(1)	1.946(3)[b]	1.939(2)
P–N (average)	1.678(8)	1.695(4)	1.677(3)
S(1a)···H(1)	2.638(25)	2.43(9)	2.513(5)
P(1)–N–P(2)	132.7(1)	126.1(4)	133.2(2)
N–P(1)–S(1)	115.5(1)	109.6(3)	114.0(1)
N–P(2)–S(2)	114.6(1)	113.4(3)	107.9(1)
N(1)–H(1)···S(1a)	178(3)	156(6)	175.9(4)
S(1)P(1)N/S(2)P(2)N (dihedral angle)	42.9[c]	35.4	3.1[c]
Deviations from S(1)P(1)N plane			
P(2)	−1.143	0.551	−0.003
S(2)	−1.616	−0.054	−0.091
Torsion angles			
S(1)P(1)NP(2)	112.7	156.2	−179.9
S(2)P(2)NP(1)	62.5	45.1	−3.1
S(1)P(1)NH(1)	−48.7	−11.6	−0.2
S(2)P(2)NH(1)	−137.0	−147.3	177.2

[a] For the Me_2PS group. [b] For the Ph_2PS group. [c] Calculated from published atomic coordinates.

those of the corresponding sodium salt and the methyl esters.[13,16,17] The spectral characteristics of the potassium salt, $K[(SPMe_2)(SPPh_2)N]$, are very similar to those of the sodium analog. In addition both the free acid and the potassium salt were characterized by ^{13}C NMR spectroscopy. The ^1H and ^{13}C NMR spectra of $NH(SPMe_2)(SPPh_2)$ show the expected resonances for the organic groups attached to phosphorus, split into two components due to the phosphorus–proton and –carbon couplings. The presence of two different phosphorus atoms in the molecular unit is not reflected in the ^1H or ^{13}C spectra of the free acid. By contrast, the ^{13}C spectrum of the potassium salt shows a doublet signal for the methyl carbons [δ(CD_3OD) 27.96, ^1J(PC) 67.9 Hz], but a resonance for aromatic *ipso*-carbon atoms with the expected doublet of doublets pattern [δ(CD_3OD) 143.54, ^1J(PC) 106.6, ^3J(PC) 5.7 Hz].[10] The non-equivalence of the two phosphorus atoms in $NH(SPMe_2)(SPPh_2)$ is clearly reflected by the two ^{31}P resonances, which exhibit a doublet pattern due to the phosphorus–phosphorus coupling [^2J(PP) 22.8 Hz].

The mass spectral data confirm the identity of the $[Co\{(SPMe_2)(SPPh_2)N\}_2]$ complex. Its electronic spectrum was recorded in $CHCl_3$ solution and is consistent with a tetrahedral co-ordination geometry. Absorption maxima were observed at 15 974, 14 184 and 13 193 (shoulder) cm^{-1}, characteristic for cobalt(II) d–d transitions.[18] A charge-transfer (CT) band also appears as a broad shoulder at 32 573 cm^{-1}.

The crystal and molecular structure of both the free acid and the cobalt(II) complex were investigated by single-crystal X-ray diffractometry. In the subsequent discussion they are compared with the previously described structures of symmetric bis(thiophosphinoyl)amines and related neutral or ionic cobalt(II) derivatives containing CoS_4 cores, respectively.

Crystal structure of $NH(SPMe_2)(SPPh_2)$

Selected bond distances and angles in $NH(SPMe_2)(SPPh_2)$ are listed in Table 2 and Fig. 1 shows the ORTEP-like view of the molecular structure with the atom numbering scheme.

The phosphorus–sulfur [P(1)–S(1) 1.962(3), P(2)–S(2) 1.946(3) Å] and –nitrogen [P(1)–N 1.698(7), P(2)–N 1.692(6) Å] distances within the SPNPS skeleton of $NH(SPMe_2)(SPPh_2)$ are typical for double P=S and single P–N bonds [*cf.* the methyl ester, $MeSPPh_2{=}NPPh_2{=}S$: P=S 1.956(3), P–S(Me) 2.069(3), P=N 1.568(4), P–N 1.610(4) Å][19] and the PNP system is bent [P(1)–N–P(2) 126.1(4)°]. Like the symmetric analogs, $NH(SPR_2)_2$ (R = Me[4] or Ph[12,20,21]) the molecule of $NH(SPMe_2)(SPPh_2)$ displays an *anti* conformation of the sulfur atoms and contains an acidic proton bound to nitrogen. However, important differences accompany the change in organic groups attached to phosphorus. Some comparative data for the three dithio derivatives are listed in Table 3. For example, the SPN(H)PS skeleton is non-planar in $NH(SPPh_2)_2$ and $NH(SPMe_2)(SPPh_2)$ (see the torsion angles given in Table 3) with a S(1)P(1)N/S(2)P(2)N dihedral angle of about 35–43°, while it is basically planar in $NH(SPMe_2)_2$. The reasons for the different conformations in these three dithioacids are not yet understood, but packing forces might be involved.

In the crystal all three dithio acids are associated through intermolecular N–H···S(=P) hydrogen bonds involving only one of the sulfur atoms of each molecule. As a consequence, the phosphorus–sulfur double bond participating in the hydrogen bonding is slightly elongated (Table 3).

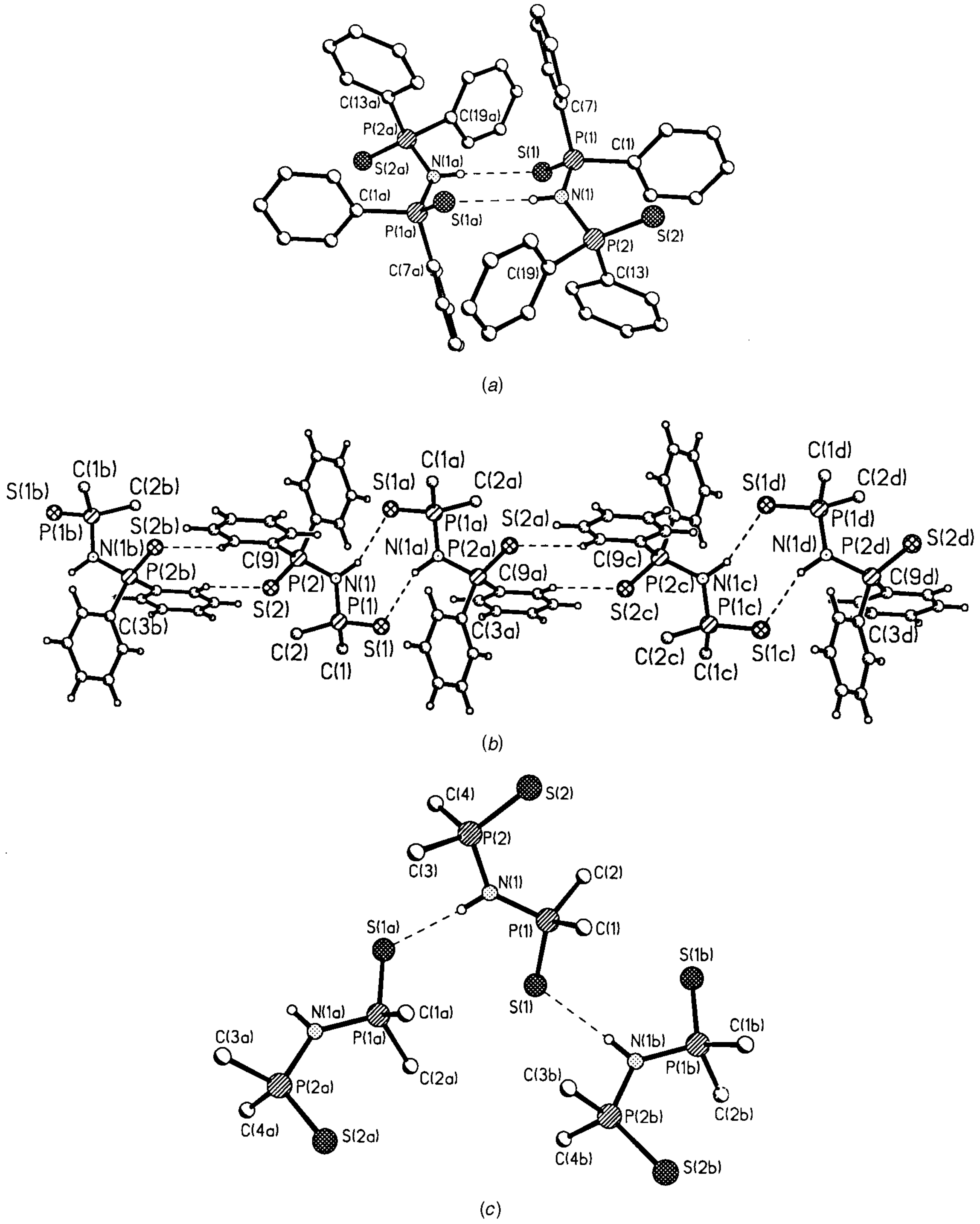


Fig. 2 View of the dimeric and polymeric associations in the crystals of (*a*) $NH(SPPh_2)_2$, (*b*) $NH(SPMe_2)(SPPh_2)$ and (*c*) $NH(SPMe_2)_2$

Important differences are observed in the lattice of $NH(SPR_2)(SPR'_2)$ acids. Thus for R = R′ = Me the molecules are associated through intermolecular N–H · · · S(=P) hydrogen bonds into chain-like polymers [Fig. 2(*c*)], while discrete dimers are found for R = R′ = Ph [Fig. 2(*a*)] and R = Me, R′ = Ph derivatives [Fig. 2(*b*)]. In addition, in the latter case the dimers are further associated into polymeric chains through interactions between the second sulfur atom of the molecular unit and an aromatic proton of a neighbouring acid molecule [S(2) · · · H(17b) 2.869 Å].

Crystal structure of $[Co\{(SPMe_2)(SPPh_2)N\}_2]$

Selected bond distances and angles in $[Co\{(SPMe_2)(SPPh_2)N\}_2]$ are listed in Table 4 and Fig. 3 shows an ORTEP-like view of the molecular structure with the atom numbering scheme.

The crystal of the cobalt complex contains discrete $[Co\{(SPMe_2)(SPPh_2)N\}_2]$ molecules, in which both ligands act as bidentate moieties. Although different organic groups are attached to phosphorus atoms of each ligand unit the cobalt–sulfur distances are equivalent [average Co–S 2.32(1) Å]. The compound can be described as a spiro-bicyclic structure, with cobalt as the spiro atom. The slightly distorted tetrahedral arrangement of sulfur atoms around the metal is reflected in the magnitude of the S–Co–S angles [range 102.7(1)–117.7(2)°], the S · · · S non-bonding distances [range 3.633(5)–3.968(5) Å] and the dihedral angles between pairs of CoS_2 planes: CoS(1)S(2)/CoS(3)S(4) 88.7, CoS(1)S(3)/CoS(2)S(4) 86.9 and CoS(1)S(4)/CoS(2)S(3) 99.4°. The structural parameters of the CoS_4 core are very similar to those observed for the related $[Co\{(SPMe_2)_2N\}_2]$ neutral complex (Table 5; and S · · · S non-bonding distances 3.619–3.878 Å, calculated from published atomic coordinates).[4] They also compare very well to those of the CoS_4 core in the $[Co(SAsMe_3)_4]^{2+}$ cation or in the $[Co(SPh)_4]^{2-}$ anion {Table 5; S···S non-bonding distances 3.563–3.972 Å in the blue isomer of $[Co(SAsMe_3)_4][ClO_4]_2$,[22] and 3.464–4.005 Å in $[N(C_6H_{11})_2H_2]_2[Co(SPh)_4]$,[18] calculated from published atomic coordinates].[18,21,22] Similar tetrahedral CoS_4 cores were reported for $[PPh_4]_2[Co(SPh)_4]$,[23] $[Me_3NCH_2CONH_2]_2[Co(SPh)_4]$[24] and $[NMe_4]_2[Co(SPh)_4]$.[25] However, a significant flattening of the idealized regular co-ordination tetrahedron was noted in the case of the green isomer of $[Co(SAsMe_3)_4][ClO_4]_2$ (Table 5, and S···S non-bonding distances 3.236–4.001 Å)[22] and the related thiourea complexes $[Co\{SC(NH_2)_2\}_4][NO_3]_2$[26,27] and $[Co\{SC(NHEt)_2\}_4][ClO_4]_2$.[28]

To allow chelate ring closure in $[Co\{(SPMe_2)(SPPh_2)N\}_2]$ the SPNPS fragment must change its conformation, bringing the sulfur atoms from the *anti* orientation in the free acid to a *syn* orientation with respect to the PNP system. As a result the S–P–N and P–N–P angles differ slightly from those in the free acid. The six-membered CoS_2P_2N inorganic rings thus formed contain equal P–S [average 2.031(5)] and P–N [average 1.59(1) Å] bonds, of intermediate magnitude between single and double phosphorus–sulfur and –nitrogen bonds, respectively [see above discussion of the $NH(SPMe_2)(SPPh_2)$ molecular structure]. Compared to the free acid, while the phosphorus–sulfur bonds are elongated, the phosphorus–nitrogen bonds are strengthened, to keep a considerable double-bond character of both bond types (Table 4). The cobalt–sulfur distances in both tetrahedral $[Co\{(SPR_2)(SPR'_2)N\}_2]$ are significantly larger (*ca.* 2.32 Å) than in the square-planar $[Co\{(SCMe)_2CH\}_2]$ complex (*ca.* 2.17 Å) (Table 5).

Despite the averaging in bond lengths, suggesting at least some delocalization of π electrons over the SPNPS fragment, achieved by chelate formation, the CoS_2P_2N rings are not

Table 4 Selected interatomic distances (Å) and angles (°) in $[Co\{(SPMe_2)(SPPh_2)N\}_2]$

Co–S(1)	2.313(4)	Co–S(3)	2.337(4)
Co–S(2)	2.322(4)	Co–S(4)	2.315(4)
P(1)–S(1)	2.035(5)	P(3)–S(3)	2.024(5)
P(2)–S(2)	2.032(5)	P(4)–S(4)	2.031(5)
P(1)–N(1)	1.58(1)	P(3)–N(2)	1.60(1)
P(2)–N(1)	1.59(1)	P(4)–N(2)	1.600(9)
S(1)···S(2)*	3.830(5)	S(3)···S(4)*	3.826(5)
S(1)–Co–S(2)	111.5(1)	S(3)–Co–S(4)	110.6(1)
S(1)–Co–S(3)	102.7(1)	S(2)–Co–S(4)	117.7(2)
S(1)–Co–S(4)	106.7(1)	S(2)–Co–S(3)	106.7(1)
S(1)–P(1)–N(1)	116.9(4)	S(3)–P(3)–N(2)	115.1(4)
S(1)–P(1)–C(1)	105.4(5)	S(3)–P(3)–C(15)	109.8(5)
S(1)–P(1)–C(2)	107.8(5)	S(3)–P(3)–C(16)	107.6(5)
N(1)–P(1)–C(1)	107.8(6)	N(2)–P(3)–C(15)	112.6(6)
N(1)–P(1)–C(2)	111.8(6)	N(2)–P(3)–C(16)	106.0(6)
C(1)–P(1)–C(2)	106.6(8)	C(15)–P(3)–C(16)	105.1(7)
S(2)–P(2)–N(1)	117.6(4)	S(4)–P(4)–N(2)	117.3(4)
S(2)–P(2)–C(3)	108.9(4)	S(4)–P(4)–C(17)	110.7(4)
S(2)–P(2)–C(9)	106.6(4)	S(4)–P(4)–C(23)	106.1(4)
N(1)–P(2)–C(3)	110.9(5)	N(2)–P(4)–C(17)	110.4(5)
N(1)–P(2)–C(9)	106.9(5)	N(2)–P(4)–C(23)	107.1(5)
C(3)–P(2)–C(9)	105.1(5)	C(17)–P(4)–C(23)	104.2(6)
P(1)–N(1)–P(2)	133.3(7)	P(3)–N(2)–P(4)	128.5(6)
Co–S(1)–P(1)	99.9(2)	Co–S(3)–P(3)	99.9(2)
Co–S(2)–P(2)	105.1(2)	Co–S(2)–P(2)	106.0(2)

* Non-bonding distance.

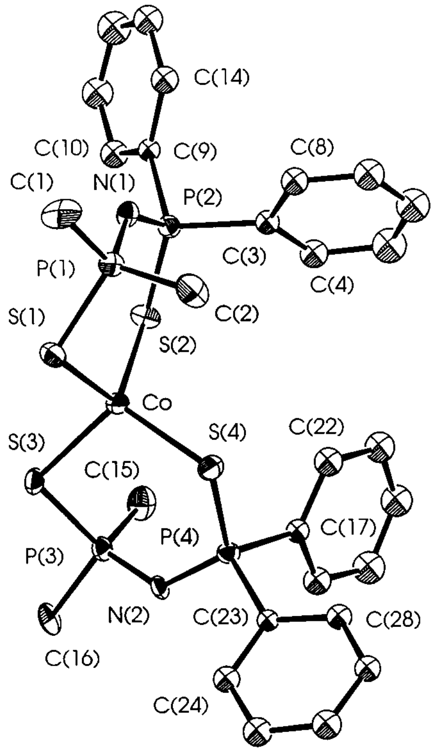


Fig. 3 An ORTEP-like drawing of the monomeric $[Co\{(SPMe_2)(SPPh_2)N\}_2]$

Table 5 Comparative structural data (bond lengths in Å, angles in °) in $[Co\{(SPMe_2)(SPPh_2)N\}_2]$ and related CoS_4 core-containing derivatives[a]

	$[Co\{(SPPh_2)(SPMe_2)N\}_2]$ (this work)	$[Co\{(SPMe_2)_2N\}_2]$ (ref. 4)	$[Co(SAsMe_3)_4][ClO_4]_2$[22]		$[N(C_6H_{11})_2H_2]_2[Co(SPh)_4]$ (ref. 18)	$[Co\{(SCMe)_2CH\}_2]$ (ref. 3)
			blue isomer	green isomer		
CoS_4 core geometry[b]	*T*	*T*	*T*	*T*	*T*	*SP*
Co–S (average)	2.32(1)	2.314(7)	2.30(1)	2.30(1)	2.328(11)	2.166(3)
S···S bite (average)	3.828(3)	3.79(1)				3.242(6)
S–Co–S (endocyclic, average)	111.1(6)	110.0(5)	—[c]	—[d]	—[e]	96.9(2)
S–Co–S (exocyclic, range)	102.7(1)–117.7(2)	103.0(1)–114.3(1)				83.1(2)
CoS(1)S(2)/CoS(3)S(4)	88.7	84.6	86.4	70.4	84.3	0.0
CoS(1)S(3)/CoS(2)S(4)	86.9	86.8	81.8	89.8	75.9	
CoS(1)S(4)/CoS(2)S(3)	88.4	92.2	78.3	109.8	81.5	
Co–S–P (average)	102.7(3.3)	102.1(1.0)				118.7(5)[f]

[a] Estimated standard deviations (e.s.d.s) for average bond lengths are calculated from the equation $\sigma = \{[\sum_{i=1}^{i=N} (x_i - x)^2/(N-1)]^{\frac{1}{2}}$, where x_i is *i*th bond length and *x* the mean of the *N* equivalent bond lengths. An analogous formula is used for the calculation of e.s.d.s for average bond angles.[9] [b] *T* = Tetrahedral, *SP* = square planar. [c] S–Co–S range 102.0(4)–120.4(4)°. [d] S–Co–S range 89.7(3)–121.0(3)°. [e] S–Co–S range 95.6(2)–121.3(2)°. [f] Co–S–C angle.

planar. Both exhibit a slightly twisted chair conformation, a behavior which contrasts with that observed for the related [Co{$(SPMe_2)_2N$}$_2$] complex where the CoS_2P_2N rings display different twisted-boat conformations.

The structural changes observed in the cobalt(II) and nickel(II) complexes of $NH(SPR_2)(SPR'_2)$ ligands are consistent with a high flexibility of the SPNPS fragment, the same ligand moiety being able to accommodate the requirements of various metal co-ordination geometries.

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