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Crystal and molecular structures of $(OPPh_2)(SPPh_2)NH$ and its sodium salt $[Na\{(OPPh_2)(SPPh_2)N\} \cdot 2THF]_2$†

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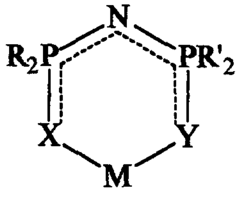
Abstract—A new method of synthesis, i.e. the reaction between $Li[HN(S)PPh_2]$ and $Ph_2P(O)Cl$ in a diethyl ether/*n*-hexane mixture, was used for the preparation of tetraphenylmonothioimidodiphosphinic acid. Its sodium salt was obtained by reacting the free acid with NaH in THF. The solid state structures of both compounds were determined by X-ray crystallography. $(OPPh_2)(SPPh_2)NH$ (**1**) contains two independent molecules in the unit cell. Both molecules exhibit an anti conformation of the chalcogen atoms in the OPNPS system. In the crystal the molecules of **1** are associated into polymeric chains through hydrogen bonds involving only the oxygen atoms of each molecule [av. (N—)H···O 2.09 Å]. The sodium salt of this acid can be considered to be built up of centrosymmetric dimers $[Na\{(OPPh_2)(SPPh_2)N\} \cdot 2THF]_2$(**2**). The O atom of the ligand unit acts as a bridging atom between the two Na atoms of the dimer [Na(1)—O(1) 2.245(9), Na(1)—O(1)′ 2.396(9) Å]. In addition Na(1) is also coordinated by the S(1)′ atom [Na(1)—S(1)′ 2.975(6) Å] and the oxygen atoms of two THF molecules [Na(1)—O(2) 2.37(1), Na(1)—O(3) 2.35(1) Å]. This results in a trigonal bipyramidal geometry around sodium atoms [O(1)′ and O(3) in axial positions for Na(1), O(3)—Na(1)—O(1)′ 171.5(4)°], and a tricyclic system with a central planar four-membered Na_2O_2 ring. © 1997 Elsevier Science Ltd

Keywords: thiophosphorus ligand, tetraphenylmonothioimidodiphosphinic acid, supramolecular, sodium.

The investigation of metallacycle-containing compounds of the type (**a**) has received increasing attention in the last years [1,2]. Most of the research interest concerned compounds containing the same chalcogen atoms and phenyl groups attached to the phosphorous atoms (i.e. $X = Y =$ O, S, or Se; $R = R' =$ Ph).



X, Y = O, S, Se

a

So far, little work has been done on $(XPR_2)(YPR'_2)NH$ ligands containing different organic groups and/or chalcogen atoms, and their metal compounds, respectively, although some early reports of Schmidpeter *et al.* [3,4] described the synthesis of such ligands and later, Siiman *et al.* [5,6] reported on the spectroscopic behavior of Ni^{II} and Cu^{II} complexes containing $[(OPPh_2)(SPPh_2)N]^-$. Only recently the molecular structures of some metal complexes con-

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† Dedicated to Professor Ionel Haiduc on the occasion of his 60th birthday.

taining $[(OPPh_2)(YPPh_2)N]^-$ (Y = S, Se) were determined by X-ray diffractometry and revealed interesting aspects concerning the coordination patterns and the conformation of the six-membered $MOYP_2N$ inorganic ring [7–10]. The molecular structure of the $Pd[\{OP(OPh)_2\}\{SP(OPh)_2\}N]_2$ complex, which provides the first example of coordination through nitrogen and sulfur for this type of ligand, was also reported [11].

We report here a new method for the synthesis of the known asymmetric ligand $(OPPh_2)(SPPh_2)NH$, its molecular structure, as well as that of the sodium salt, $[Na\{(OPPh_2)(SPPh_2)N\} \cdot 2THF]_2$. During the preparation of this manuscript, a report on the molecular structure of $(OPPh_2)(SPPh_2)NH \cdot 0.3H_2O$ was published [10], but the structure was disordered and therefore the molecular parameters cannot be used for structure comparison purposes.

EXPERIMENTAL

The starting materials were prepared according to literature methods: $Ph_2P(O)Cl$ [12], $Ph_2P(S)NH_2$ [12]. IR spectra (4000–400 cm^{-1}) were recorded on KBr discs using a SPECORD 75 IR Zeiss-Jena (Germany) spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra were obtained at room temperature in $CDCl_3$/DMSO-d_6 using a VARIAN GEMINI-300 spectrometer operating at 299.5, 75.4 and 121.4 MHz, respectively. TMS and H_3PO_4 85% were used as external standards.

Preparation of tetraphenylmonothioimidodiphosphinic acid, $(OPPh_2)(SPPh_2)NH$ (**1**).

A solution of *n*-BuLi in *n*-hexane (78.6 ml 1.565 M) was added dropwise to a stirred suspension of $Ph_2P(S)NH_2$ (29.1 g, 0.125 mol) in 300 ml of anhydrous diethyl ether, under argon atmosphere. The reaction mixture was cooled to room temperature, and then a solution of $Ph_2P(O)Cl$ (14.9 g, 0.062 mol) in 100 ml of anhydrous diethyl ether was added dropwise. About 250 ml of the solvent was distilled off from the reaction mixture, 200 ml of water 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 (14.5 g, after recrystallization from toluene). The clear viscous filtrate containing the lithium salt of the title acid was treated with HCl 10% until no solid product deposited. The white solid product was collected by suction filtration and recrystallized from ethanol as colorless crystals. Yield: 24.2 g (89%), m.p. 172–174°C (lit.: [7] 172–174°C). The spectroscopic behavior (IR, ^1H, ^{13}C and ^{31}P NMR) of the sample was identical with that previously reported [7] for the same compound prepared using the method described in [4].

Preparation of sodium tetraphenylmonothioimidodiphosphinate, $Na[(OPPh_2)(SPPh_2)N]$.

A solution of $(OPPh_2)(SPPh_2)NH$ (0.43 g, 1 mmol) in 20 ml THF was added to NaH (0.024 g, 1 mmol, as 80% dispersion in paraffin oil), and the mixture was stirred for 4 h, at room temperature. The solvent was removed in vacuo, and the remaining white product was washed several times with petroleum ether. The title compound was obtained as colorless crystals after addition of *n*-hexane to a concentrated THF solution of the sodium salt. Yield: 0.42 g (73%), m.p. 180–182°C. Selected IR data (KBr, cm^{-1}): $\nu_{as}(P_2N)$ 1230 vs, $\nu(PO)$ 1140 vs, br, $\nu(PS)$ 600 vs. ^1H NMR: 7.18m [12H, $P(S)—C_6H_5$, $P(O)—C_6H_5$-*meta*+*para*], 7.74ddd [4H, $^3J_{PH}$ 12.1 Hz, $^3J_{HH}$ 7.8 Hz, $^4J_{HH}$ 1.7 Hz, $P(O)–C_6H_5$-*ortho*], 7.92 ddd [4H, $^3J_{PH}$ 13.3 Hz, $^3J_{HH}$ 6.5 Hz, $^4J_{HH}$ 3.0 Hz, $P(S)–C_6H_5$-*ortho*]; ^{13}C NMR: 126.95d ($^3J_{PC}$ 10.9 Hz, C_m), 127.10d ($^3J_{PC}$ 11.7 Hz, C_m), 128.71 d ($^4J_{PC}$ 2.8 Hz, C_p), 128.92d ($^4J_{PC}$ 2.2 Hz, C_p), 130.25d [$^2J_{PC}$ 10.9 Hz, C_o, $P(O)–C_6H_5$], 130.81d [$^2J_{PC}$ 9.5 Hz, C_o, $P(S)–C_6H_5$], 139.77 dd [$^1J_{PC}$ 132.6 Hz, $^3J_{PC}$ 5.5 Hz, C_i, $P(O)–C_6H_5$], 142.08dd [$^1J_{PC}$ 107.3 Hz, $^3J_{PC}$ 5.2 Hz, C_i, $P(S)—C_6H_5$]; ^{31}P NMR: 15.8s ($^1J_{PC}$ 132.1 Hz, Ph_2PO); 35.8s ($^1J_{PC}$ 105.3 Hz, Ph_2PS).

X-Ray crystal determinations

$(OPPh_2)(SPPh_2)NH$ (**1**). Crystals of **1**, suitable for X-ray diffraction investigation, were obtained from methanol/*n*-hexane solvent mixture using the diffusion method. Data were collected at room temperature on a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and the full-matrix least-squares refinement was performed with the SHELXTL-PC program system [13]. Details of crystal data, measurement of intensities, and data processing are summarized in Table 1. The structure was solved by Patterson method. All non-hydrogen atoms were refined anisotropically and the N–*H* atom was located from a difference map. The positions of the other hydrogen atoms were calculated as a riding model, with fixed, isotropic temperature factor $U = 0.06$ Å^2.

$[Na\{(OPPh_2)(SPPh_2)N\} \cdot 2THF]_2$ (**2**). Crystals of **2**, suitable for X-ray diffraction investigation, were obtained from THF solution on slow evaporation at 6°C. Data were collected at room temperature on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation, and the structure was solved by direct methods [14], and expanded using Fourier techniques. Details of crystal data measurement of intensities, and data processing are summarized in Table 1. The intensities of three representative reflections that were measured every 150 reflections decreases throughout data collection

Table 1. Crystal data for $(OPPh_2)(SPPh_2)NH$ (**1**) and $[Na\{(OPPh_2)(SPPh_2)N\}\cdot 2THF]_2$ (**2**)

	(**1**)	(**2**)
Formula	$C_{24}H_{21}NOP_2S$	$C_{32}H_{36}O_3NP_2SNa$
FW	433.4	500.64
Crystal size (mm)	0.48 × 0.24 × 0.12	0.30 × 0.34 × 0.32
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a (Å)	8.757(1)	13.104(4)
b (Å)	10.423(2)	13.602(8)
c (Å)	24.199(5)	11.632(6)
α (°)	90.49(1)	115.14(4)
β (°)	98.74(1)	115.17(3)
γ (°)	91.89(1)	95.41(5)
V (Å^3)	2181.9(6)	1600(1)
Z	4	2
D_{calc} (g cm^{-3})	1.319	1.25
μ(Mo-Kα)(mm^{-1})	0.310	0.247
2θ range (°)	3-50	2-45
F (000)	904	632
Reflections collected	8242	5520
Independent reflections	7689	4184
Observed reflections	5271 $[F > 3.0\sigma(F)]$	1267 $[F_o^2 \geqslant 3\sigma(F_o)^2]$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$	$w^{-1} = \sigma^2(F_o)$
R (%)	7.13^a	6.19^b
R' (%)	6.57^a	5.27^b
GOF	1.48	1.85

^{a} $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = wR = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$; $S = [\Sigma w\Delta^2/(N_o\text{-}N_p)]^{1/2}$; $\Delta = F_o - F_c$.
^{b} $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = wR = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$; $S = [\Sigma\Delta/\sigma]/(N_o\text{-}N_p)$; $\Delta = F_o - F_c$.

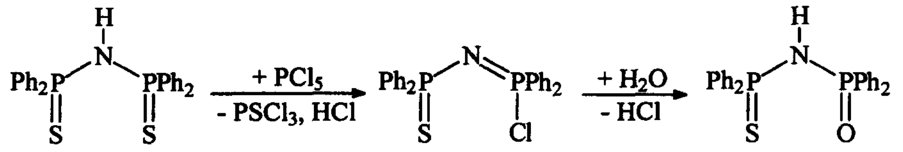
indicating decay of the crystal (43%) so a decay correction was applied. All calculations were performed using the TEXSAN[15] crystallographic software package of Molecular Structure Corp. Only the sulfur and phosphoros atoms were refined anisotropically. The hydrogen atoms were included in their idealized positions with C–H set at 0.95 Å and the isotropic thermal parameters of all hydrogen atoms were set at 1.2 times that of the atom to which they were attached.

RESULTS AND DISCUSSION

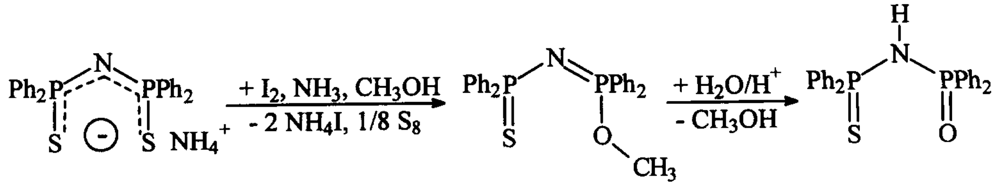
The first synthesis of tetraphenylmonothioimidodiphosphinic acid, $(OPPh_2)(SPPh_2)NH$, reported by Schimdpeter *et al.* [4] was based on the partial oxidation of the dithio derivative according to the schemes (1) or (2).

Recently another method, based on the oxidation of the monooxide $(OPPh_2)(PPh_2)NH$ with elemental sulfur [equation (3)], was also reported [10].

We prepared the same compound according the scheme (4), by reacting the lithiated amide Li[HN(S)PPh_2] with the diphenylphosphinyl chloride $Ph_2P(O)Cl$ in a diethyl ether/*n*-hexane mixture. Since BuLi is soluble in diethyl ether, its use instead of *tert*-BuOK [3,16] allows a better contact between the reactants and improves considerably the yield. 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 $(XPR_2)(YPR'_2)NH(X = O, S; R, R' = Me, Ph)$ were already prepared in our lab and characterized by X-ray diffractometry [17], and work is in progress to prepare similar derivatives containing selenium as a second chalcogen atom.



(1)



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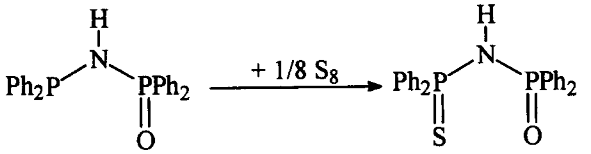

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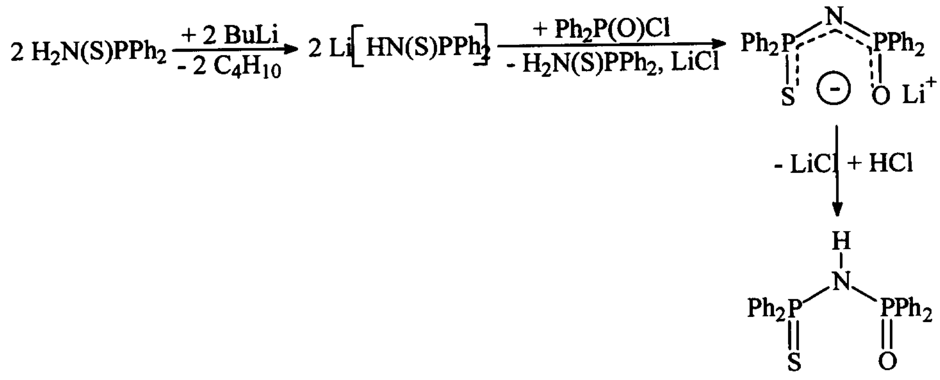

(4)

The corresponding sodium salt was obtained by reacting the free acid with NaH in THF. The compound was characterized by IR and multinuclear NMR (see the Experimental section). The solid state structures of both $(OPPh_2)(SPPh_2)NH$ and its Na salt were determined by X-ray diffraction.

The strong infrared absorptions observed for the Na salt at 1230, 1140 and 600 cm^{-1} were assigned to $\nu_{as}(P_2N)$, $\nu(PO)$ and $\nu(PS)$ stretching vibrations, respectively, by comparison with the spectra of the free acid and the corresponding K salt [7].

The ^{31}P NMR spectrum of $Na[(OPPh_2)(SPPh_2)N]$ exhibits two resonances at 15.8 ($Ph_2P{=}O$) and 35.8 ppm ($Ph_2P{=}S$), the phosphoros–phosphoros coupling being not observed. The assignment of these resonances was confirmed by the magnitude of the phosphorus–carbon couplings. Both the ^1H and ^{13}C spectra showed two groups of signals in the aromatic region (with the expected doublet pattern due to phosphorus-proton and phosphorus-carbon couplings, respectively), corresponding to the phenyl groups attached to different phosphorus atoms. The resonances of ipso carbon atoms exhibit a doublet pattern due to the $^1J_{PC}$ and $^3J_{PC}$ couplings.

The crystal and molecular structure of $(OPPh_2)(SPPh_2)NH$ (**1**)

For **1** the unit cell contains two independent, but very similar, molecules. Selected bond distances and angles for both molecules **1a** and **1b** are listed in Table 2 and Fig. 1 shows the ORTEP-like view of their structure, with the atom numbering scheme.

In the molecular unit the P—N—P system is angular [P—N—P 131.4(3) and 132.9(3)° in **1a** and **1b**, respectively]. The SPNPO skeleton has an anti conformation, with an interatomic non-bonding S···O distance of about 5.5 Å. The dihedral angles SPN/OPN are 51.5° for **1a** and 50.8° **1b**. In the molecule of **1** the acid hydrogen atom is linked to the nitrogen atom [N(11)—H(11) 0.87(6) Å for **1a**, and N(21)—H(21) 0.86(6) Å for **1b**]. The phosphorus–sulfur [av. 1.925(14) Å] and phosphorus-oxygen [av. 1.503(16) Å] bond lengths in **1** are typical for P═S and P═O double bonds, respectively [cf. $Ph_2P({=}S)SH$ [18]: P═S 1.954(1) Å, P—S 2.077(1) Å; $Ph_2P(O)OH$ [19]: P═O 1.486(6) Å, P—O 1.526(6) Å] and similar to those observed for the symmetric derivatives: P═S 1.936(1), 1.950(1) Å in $(SPPh_2)_2NH$ [20], and P═O 1.519(2) Å in '$(OPPh_2)_2NH$' [20] (see subsequent comments on the polymeric association in the dioxo compound). The phosphorus–nitrogen bonds in the molecular unit are equivalent regardless the nature of the chalcogen atom attached to phosphorus, and their magnitude [av. 1.680(12) Å] is clearly consistent with P—N single bonds [cf. $(Me_3Si)_2N{-}P({=}NBu^t)S]_2$ [21]: P═N 1.529(2) Å, P—N 1.662(2) Å; $Ph_2P({=}S){-}N{=}P({-}SMe)Ph_2$ [22]: P═N 1.568(4) Å, P—N 1.610(4) Å]. However, the

Table 2. Interatomic distances (Å) and angles (°) in $(OPPh_2)(SPPh_2)NH$ (**1**)

Molecule **1a**		Molecule **1b**	
P(11)—S(11)	1.935(2)	P(21)—S(21)	1.915(2)
P(11)—N(11)	1.694(4)	P(21)—N(21)	1.673(5)
P(12)—N(11)	1.668(5)	P(22)—N(21)	1.683(5)
P(12)—O(11)	1.491(4)	P(22)—O(21)	1.514(4)
N(11)—H(11)	0.87(6)	N(21)—H(21)	0.86(6)
S(11)—P(11)—N(11)	115.7(2)	S(21)—P(21)—N(21)	115.2(2)
S(11)—P(11)—C(11)	113.1(2)	S(21)—P(21)—C(71)	113.5(2)
S(11)—P(11)—C(21)	113.8(2)	S(21)—P(21)—C(81)	114.0(2)
N(11)—P(11)—C(11)	103.8(2)	N(21)—P(21)—C(71)	102.8(2)
N(11)—P(11)—C(21)	105.5(2)	N(21)—P(21)—C(81)	105.7(2)
C(11)—P(11)—C(21)	103.6(2)	C(71)—P(21)—C(81)	104.5(2)
O(11)—P(12)—N(11)	113.5(2)	O(21)—P(22)—N(21)	112.6(2)
O(11)—P(12)—C(31)	112.5(2)	O(21)—P(22)—C(51)	114.2(2)
O(11)—P(12)—C(41)	112.8(2)	O(21)—P(22)—C(61)	112.0(2)
N(11)—P(12)—C(31)	108.1(2)	N(21)—P(22)—C(51)	107.4(2)
N(11)—P(12)—C(41)	105.1(2)	N(21)—P(22)—C(61)	103.9(3)
C(31)—P(12)—C(41)	104.2(2)	C(51)—P(22)—C(61)	106.0(3)
P(11)—N(11)—P(12)	131.4(3)	P(21)—N(21)—P(22)	132.9(3)
P(11)—N(11)—H(11)	111(4)	P(21)—N(21)—H(21)	108(4)
P(12)—N(11)—H(11)	114(5)	P(22)—N(21)—H(21)	113(4)

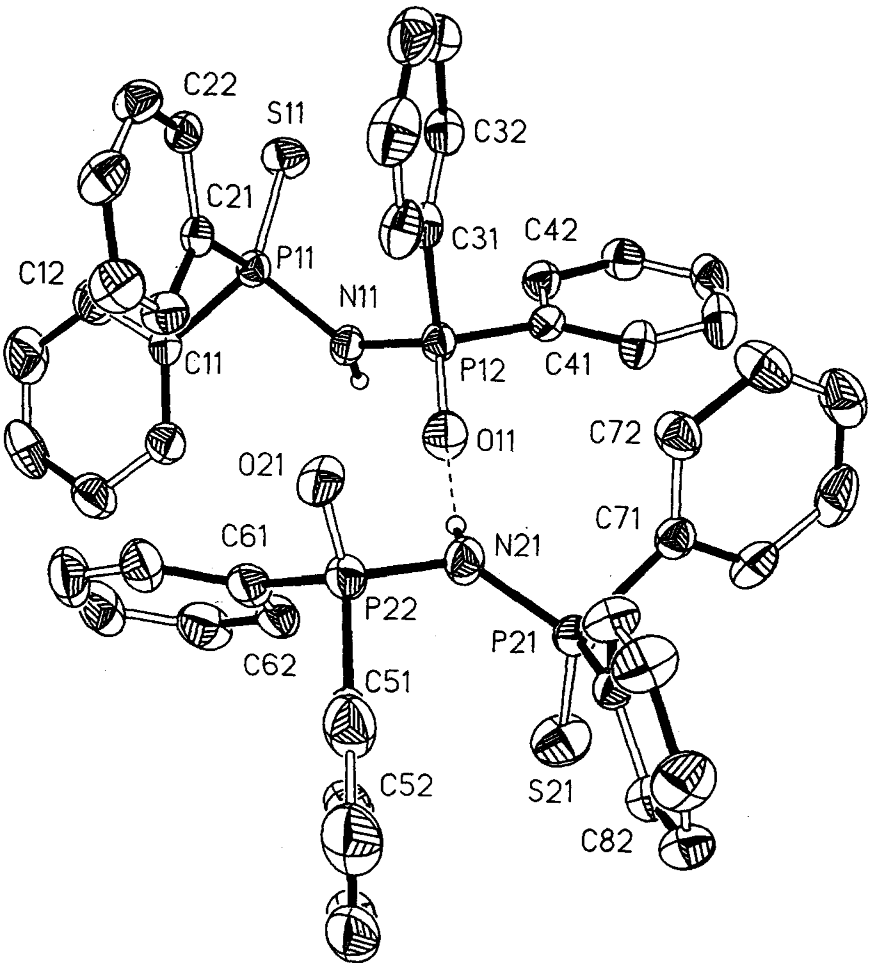

Fig. 1. ORTEP plot of $(OPPh_2)(SPPh_2)NH$, showing both molecules **1a** and **1b**. For clarity only the hydrogen atoms at nitrogens are shown.

sum of the angles at the N atom is close to 360° [for example in **1a**: P(11)—N(11)—P(12) 131.4(3)°, P(11)—N(11)—H(11) 111(4)°, P(12)—N(11)—H(11) 114(5)°], thus suggesting considerable sp^2 character [similar behavior was observed for the symmetric analogs, $(SPPh_2)_2NH$ [20,23], and $(SePPh_2)_2NH$ [24]]. The tetrahedral geometry around both phosphorus atoms in the molecular unit is distorted as reflected by the angles listed in Table 2.

In the crystal the $(OPPh_2)(SPPh_2)NH$ molecules are associated into polymeric chains through H bonds that involve only the O atoms of each molecular moiety [O(21)···H(11) 2.15(6) Å, N(11)···O(21) 3.024(5) Å, N(11)—H(11)···O(21) 173(5)° for molecule **1a**, and O(11a)···H(21) 2.03(6) Å, N(21)···O(11a) 2.886(7) Å, N(21)—H(21)···O(11a) 175(5)° for molecule **1b**—the symmetry code for intermolecular bond O(11a)···H(21) is $x, y, z \rightarrow 1+x, y, z$] (Fig. 2).

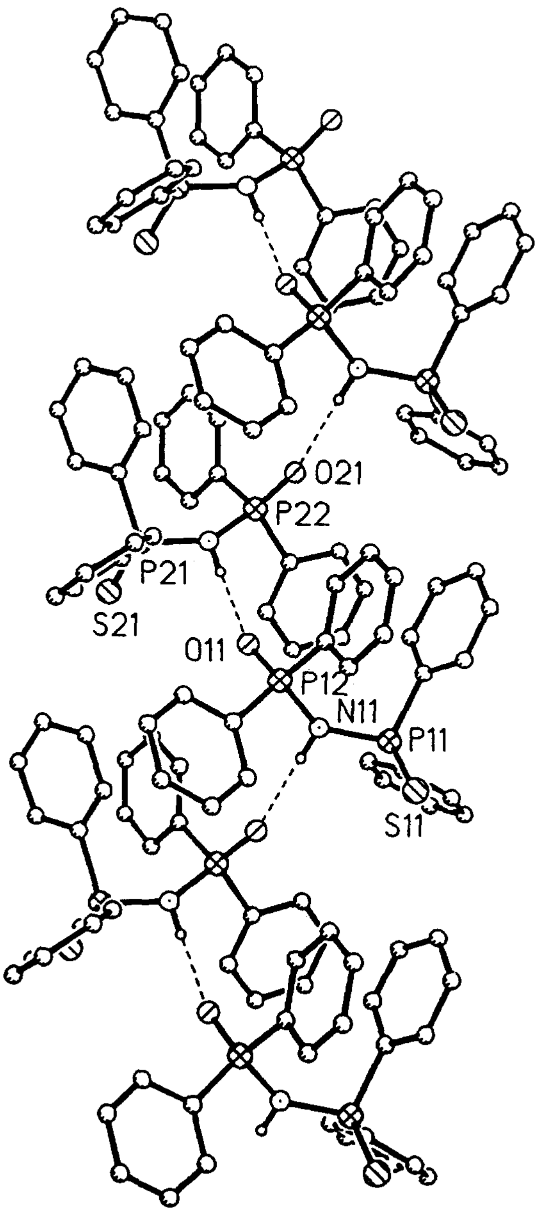

Fig. 2. Chain polymeric association through H bonding in $[(OPPh_2)(SPPh_2)NH]_n$.

This contrasts to the behavior of the symmetric phenyl analogs $(SPPh_2)_2NH$ [20,23] (Fig. 3b) and $(SePPh_2)_2NH$ [24] which exhibit dimeric associations through N—H···S bonds, but resembles the association observed for the symmetric alkyl derivatives $(SPMe_2)_2NH$ [25] (Fig. 3c) and $(SPPr^i_2)_2NH$ [26]. It should be mentioned here that dioxo derivative, '$(OPPh_2)_2NH$' [20], shows a completely different chain polymeric structure structure (Fig. 3a), with a linear P—N—P fragment, planar OPNPO skeleton and strong, symmetric O—H—O hydrogen bonds (for comparative structural data of the aryl derivatives see Table 3). The lengths of the H···O bond in $(OPPh_2)(SPPh_2)NH$ [O(21)···H(11) 2.15(6) Å for **1a**, and O(11a)···H(21) 2.03(6) Å for **1b**] are significantly larger than those observed in the dioxo derivative [H—O 1.196(2) Å] [20] and $Ph_2P(O)OH$ [H···O 1.30(7) Å] [19], respectively.

The crystal and molecular structure of $[Na\{(OPPh_2)(SPPh_2)N\}\cdot 2THF]_2$ (**2**)

Selected bond distances and angles for **2** are listed in Table 4 and Fig. 4 shows the structure, with the atom numbering scheme. In the Na salt the P—N—P system is again angular [P(1)—N(1)—P(2) 130.8(6)°] as it is in the free acid, but the SPNPO skeleton has a syn conformation, with a dihedral angle SPN/OPN of 42.9° and a nonbonding distance O(1)···S(1) of about 3.709 Å. Within the ligand moiety the phosphorus-oxygen distance is of the same magnitude as in the free acid, but the phosphorus–sulfur distance is significantly longer [P(2)—S(1) 1.979(4) Å in (**2**), and av. P—S 1.925(14) Å in (**1**)]. In contrast the phosphorus-nitrogen bonds are significantly shorter [P—N 1.577(9), 1.606(9) Å in (**2**), and av. P—N 1.680(12) Å in (**1**)], suggesting an increase in double bond character as a result of π delocalization.

In the monomeric unit, the Na(1) is coordinated only by the oxygen atom of the corresponding ligand moiety [Na(1)—O(1) 2.245(9) Å; c.f. the sum of the van der Waals radii is Σ_{vdW}(Na,O) = 3.80 Å [28]], while the sulfur atom S(1) is too far to be involved in an interaction with this metal atom [Na(1)···S(1) 5.07 Å; c.f. the sum of the van der Waals radii is Σ_{vdW} (Na,S) = 4.10 Å [28]]. In addition, Na(1) is also coordinated by the oxygen atoms of two THF molecules at distances significantly longer than Na(1)—O(1) distance. In the crystal, discrete dimers of $[Na\{(OPPh_2)(SPPh_2)N\}\cdot 2THF]_2$ are formed (Fig. 5), each Na completing its coordination with an oxygen and a sulfur belonging to a neighbouring Na $[(OPPh_2)(SPPh_2)N]\cdot 2THF$ unit [Na(1)—O(1)′ 2.396(9) Å, Na(1)—S(1)′ 2.975(6) Å]. All bonding

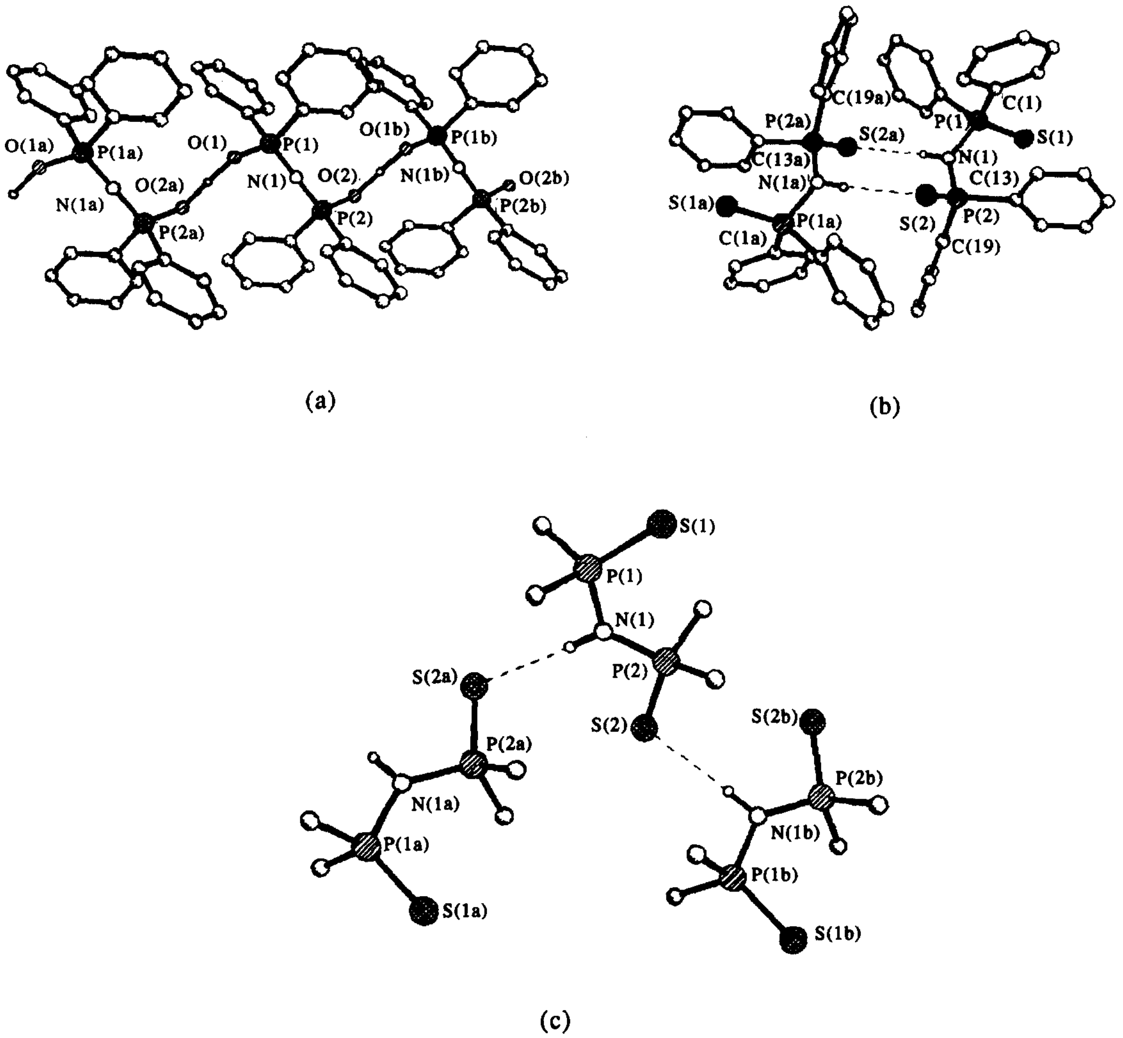

Fig. 3. Association through H bonding in (**a**) $[H\{(OPPh_2)_2N\}]_n$, (**b**) $[(SPPh_2)_2NH]_2$, and (c) $[(SPMe_2)_2NH]_n$ (redrawn using published atomic coordinates).

distances involving the metal atom are in the range of Na—O and Na—S bonds observed in related Na compounds containing oxo and thio ligands (for comparative data see Table 5). The coordination geometry around Na(1), for example, is distorted trigonal bipyramidal, with O(3) and O(1)′ in axial positions [O(3)—Na(1)—O(1)′ 171.5(4)°], and O(1), O(2) and S(1)′ in equatorial ones [deviations from the best equatorial Na(1)O(1)O(2)S(1)′ plane: Na(1) −0.014, O(1) 0.004, O(2) 0.005, S(1)′ 0.004 Å, and axial-equatorial O—Sn—X angles in the range 86.3–99.0°].

The formation of the dimer association results in an *ortho*-condensed tricyclic, carbon-free system shown in Fig. 5. The central, four-membered Na_2O_2 ring is planar, with the P and N atoms belonging to the six-membered $NaOSP_2N$ rings almost in the same plane [deviations from the Na(1)O(1)Na(1)′O(1)′ plane: P(1) −0.137, N(1) 0.130, P(1)′ 0.137, N(1)′ −0.130 Å]. The $NaOSP_2N$ rings are symmetrically folded about the Na(1) ··· N(1)′ and Na(1)′ ··· N(1) axis, respectively, on opposite sides relative to the central ring, with a dihedral angle between best NaOPN and NaSPN planes of 112.3°. This results in a ladder structure of the whole tricyclic system. The conformation of the six-membered $NaOSP_2N$ rings is reflected by the torsion angles listed in Table 4. If the PNP plane is taken as reference, the $NaOSP_2N$ ring has a chair conformation [deviations from the P(1)N(1)P(2) plane; O(1) 1.173, S(1) 1.168, Na(1)′ 2.532 Å].

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Table 3. Comparative molecular dimensions for $(XPPh_2)(YPPh_2)NH$ (X,Y = O, S, Se)[a]

	X = Y = O [20]	X = O ; Y = S[b] [this work]	X = Y = S [20]	X = Y = Se [24]
P—O	1.519(2)	1.491(4)		
P—S		1.935(2)	1.936(1) 1.950(1)[c]	
P—Se				2.085(1) 2.101(1)[c]
P—N	1.535(1)	1.681(18)[a]	1.678(9)[a]	1.682(6)[a]
O—H	1.196(2)[d]			
N—H		0.87(6)	0.807(20)	0.94
H···X		2.15(6)[e]	2.536[f,g]	2.52[h]
N···X		3.024(5)[e]	3.344[f]	3.19[h]
O—P—N	116.7(1)	113.5(2)		
S—P—N		115.7(2)	115.1(6)[a]	
Se—P—N				115.3(1.1)[a]
P—N—P	180	132.2(1.1)	132.6(1)	132.3(2)
O—H—O	180			
N—H···X		173(5)[e]	173.4[f]	166[h]
Torsion angles				
X(1)P(1)N(1)P(2)	0.0	82.1 (X=S)	112.7	110.8
X(2)P(2)N(1)P(1)	0.0	123.6 (X=O)	62.5	62.7

[a] Esd's for average bond lengths are calculated from the equation $\sigma = \left[\sum_{i=l}^{i=N} (x_i - x)^2/(N-1)\right]^{1/2}$, where x_i is ith bond length and x is the mean of the N equivalent bond lengths. An analogous formula is used for the calculation of esd's for average bond angles [27].

[b] Data for molecule **1a**;

[c] For the chalcogen atom involved in H bonding.

[d] Symmetric, liniar O—H—O system.

[e] X=O.

[f] X=S;

[g] Calculated from published atomic coordinates

[h] X = Se.

Table 4. Important bond lengths (Å) and angles (°) for $[Na\{(OPPh_2)(SPPh_2)N\}\cdot 2THF]_2$ (**2**)[a]

Na(1)—O(1)	2.245(9)	O(1)—Na(1)—O(2)	104.7(4)
Na(1)—O(2)	2.37(1)	O(1)—Na(1)—S(1)′	120.4(3)
Na(1)—O(3)	2.35(1)	O(2)—Na(1)—S(1)′	134.9(3)
Na(1)—O(1)′	2.396(9)	O(3)—Na(1)—O(1)	98.9(3)
Na(1)—S(1)′	2.975(6)	O(3)—Na(1)—O(2)	86.5(3)
		O(3)—Na(1)—S(1)′	87.8(3)
P(1)—O(1)	1.494(7)	O(1)′—Na(1)—O(1)	89.4(3)
P(1)—N(1)	1.577(9)	O(1)′—Na(1)—O(2)	92.9(3)
P(2)—N(1)	1.606(9)	O(1)′—Na(1)—S(1)′	86.7(2)
P(2)—S(1)	1.979(4)	O(3)—Na(1)—O(1)′	171.5(4)
O(1)—P(1)—N(1)	118.2(5)	S(1)—P(2)—N(1)	119.5(4)
O(1)—P(1)—C(1)	109.6(5)	S(1)—P(2)—C(13)	109.5(4)
O(1)—P(1)—C(7)	110.0(5)	S(1)—P(2)—C(19)	111.1(4)
N(1)—P(1)—C(1)	108.6(5)	N(1)—P(2)—C(13)	108.1(5)
N(1)—P(1)—C(7)	105.5(6)	N(1)—P(2)—C(19)	104.1(5)
C(1)—P(1)—C(7)	103.8(5)	C(13)—P(2)—C(19)	103.3(5)
P(1)—N(1)—P(2)	130.8(6)		
Torsion angles			
Na(1)′S(1)P(2)N(1)	−28.7	Na(1)S(1)′P(2)′N(1)′	28.7
S(1)P(2)N(1)P(1)	−42.9	S(1)′P(2)′N(1)′P(1)′	42.9
O(1)P(1)N(1)P(2)	62.4	O(1)′P(1)′N(1)′P(2)′	−62.4
N(1)P(1)O(1)Na(1)′	15.6	N(1)′P(1)′O(1)′Na(1)	−15.6
P(1)O(1)Na(1)′S(1)	−65.0	S(1)′Na(1)O(1)′P(1)′	65.0
P(2)S(1)Na(1)′O(1)	65.7	O(1)′Na(1)S(1)′P(2)′	−65.7

[a] Symmetry equivalent position (2 − x, 1 − y, 1 − z) is denoted by prime.

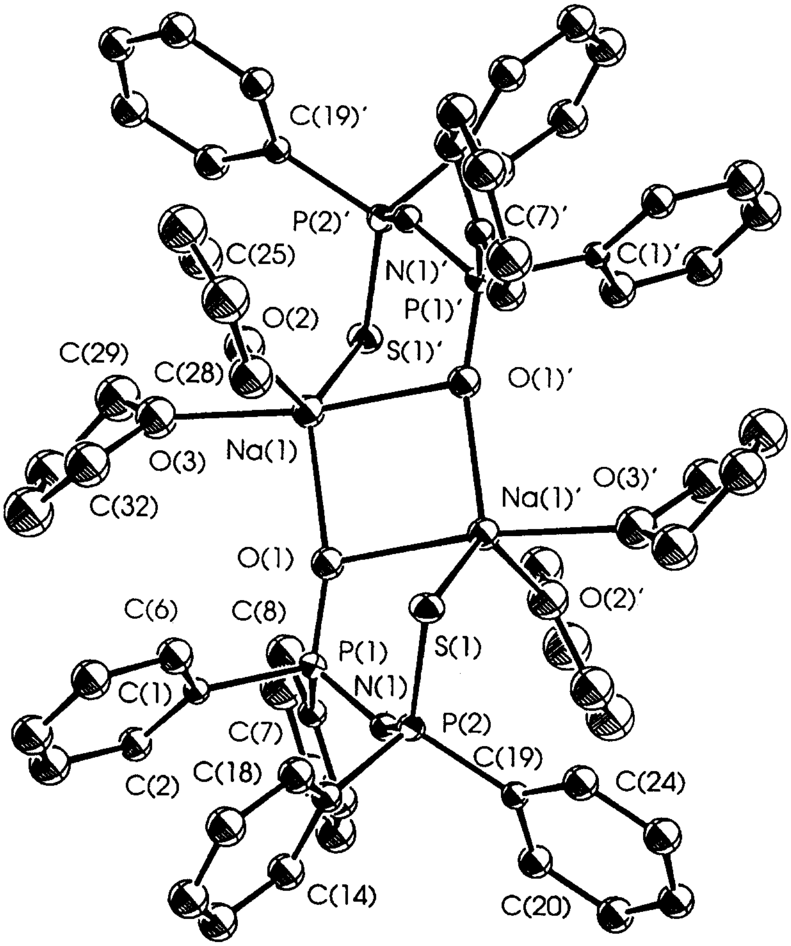

Fig. 4. View of the dimer association [Na{(OPPh$_2$)(SPPh$_2$)N} · 2THF]$_2$.

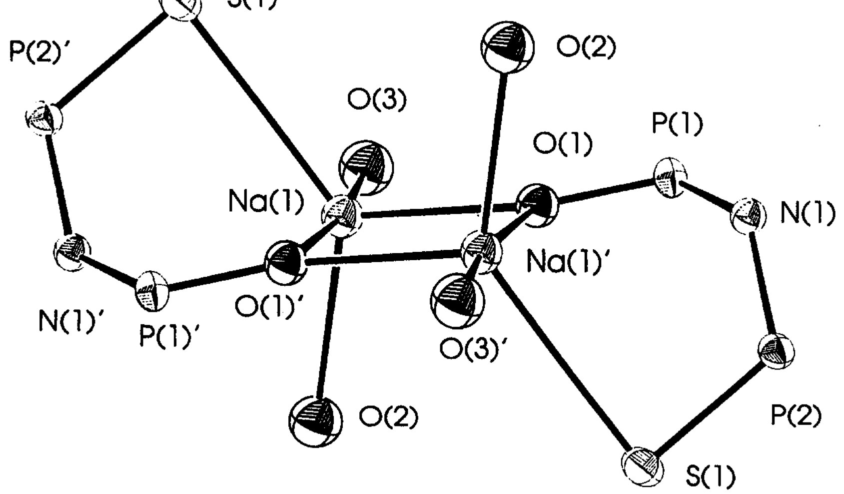

Fig. 5. View of the tricyclic system in [Na{(OPPh$_2$)(SPPh$_2$)N} · 2THF]$_2$. Carbon and hydrogen atoms are omitted for clarity.

Table 5. Comparative Na—O and Na—S bond distances in $[Na\{(OPPh_2)(SPPh_2)N\}\cdot 2THF]_2$ and some related derivatives

	Na—O (ligand)	Na—O (solvent)	Na—S	Coordination geometry at Na	Association (degree)	Ref.
$[Na\{(OPPh_2)(SPPh_2)N\}\cdot 2THF]_2$	2.245(9) 2.396(9)	2.35(1) 2.37(1)	2.975(6)	trigonal bipyramid	dimer	[this work]
$[Na(\{OP(OPh)_2\}_2N)]_6^a$	2.23 2.26 2.30 2.34 2.65			trigonal bipyramid	hexamer	[29]
$[Na\{(OCCH_3\}_2CH\}\cdot H_2O]_n^b$	2.318(1) 2.325(1) 2.382(1) 2.387(1)	2.422(1) 2.433(1)		distorted octahedral	polymer	[30]
$[Na\{OC_6H_2(CF)_3\text{-}2,4,6\}\cdot 2THF]_2^c$	2.231(6) 2.296(7)	2.306(6) 2.313(6)		distorted octahedral	dimer	[31]
$[Na\{SC_6H_2(CF)_3\text{-}2,4,6\}\cdot 2THF]_n^d$		2.263(4) 2.277(3)	2.833(2) 2.838(2)	distorted octahedral	polymer	[31]
$[Na(S_2PEt_2)\cdot 2H_2O]_n^e$		2.397(2) 2.405(2) 2.463(2) 2.496(2)	2.998(1) 3.001(1)	distorted octahedral	polymer	[32]

[a] Distances for Na(1); three different Na atoms are present in the hexamer unit: Na(2)—O (range) 2.30–2.84 Å, Na(3)—O (range) 2.23–3.05 Å.

[b] Trimetallic tetraconnective acetylacetonato ligand and bimetallic biconnective (O-bridging) H_2O molecule

[c] Bimetallic biconnective (O-bridging) phenoxo ligand, terminal THF molecules and two additional weak Na-F interactions/Na atom

[d] Two Na atoms in the asymmetric unit; Na(2)—O (THF) 2.312(4), 2.317(3) Å, Na(2)-S 2.825(2), 2.835(2) Å; bimetallic biconnective (S-bridging) thiolato ligand, terminal THF molecules and two additional weak Na-F interactions/Na atom

[e] Bimetallic biconnective (S-bridging) dithiolato ligand, involving only one sulfur atom/ligand moiety in interactions with Na atoms.

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