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Note

First nickel(II) complexes containing tetrahedral NiO_2S_2 cores. The molecular structures of $Ni[(OPPh_2)(SPR_2)N]_2$ (R = Ph, Me)

Anca Silvestru* [a,1], Danut Bîlc [a], Roland Rösler [a], John E. Drake* [b,2], Ionel Haiduc

[a] *Facultatea de Chimie, Universitatea 'Babes-Bolyai', RO-3400 Cluj-Napoca, Romania*
[b] *Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont., N9B 3P4, Canada*

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Abstract

$Ni[(OPR'_2)(SPR_2)N]_2$ complexes were obtained in good yields by reacting $NiCl_2 \cdot 6H_2O$ and the alkaline salts of the corresponding tetraorganomonothioimidodiphosphinic acids. All compounds were characterized by elemental analysis and IR. The molecular structure of $Ni[(OPPh_2)(SPR_2)N]_2$ (R = Ph, Me) has been determined by single-crystal X-ray diffractometry. $Ni[(OPPh_2)(SPPh_2)N]_2$ (**1**) crystallizes in the monoclinic space group $P2_1/c$ (no. 14), and $Ni[(OPPh_2)(SPMe_2)N]_2$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ (no. 2). The crystals of both compounds contain discrete mononuclear molecules. The asymmetric ligands act as monometallic biconnective units which results in a tetrahedral NiO_2S_2 core. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Nickel complexes; Chalcogenoimidodiphosphinato complexes; Tetrahedral complexes

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1. Introduction

The interest for the study of metal tetraorganodichalcogenoimidodiphosphinates shown by various research groups [1–5] was focused mainly on symmetrical ligands $[(XPR_2)_2N]^-$ (i.e. the same organic group and the same chalcogen atoms attached to the P atoms: R = Ph, OPh, X = O; R = Me, Pr^i, Ph, OPh, X = S; R = Ph, X = Se). In the last years, although several asymmetric ligands containing different organic groups and/or chalcogen atoms have become available, relatively few studies have been reported on complexes containing $[(XPR_2)(YPR'_2)N]^-$ moieties, i.e. $[(SPMe_2)(SPPh_2)N]^-$ [6–8], $[(SPPh_2)\{SP(OEt)_2\}N]^-$ [9], $[(OPMe_2)(OPPh_2)N]^-$ [7,10], $[(OPPh_2)\{OP(OEt)_2\}N]^-$ [11], $[(OPEt_2)\{OP(OPh)_2\}N]^-$ [12], $[(OPMe_2)(SPPh_2)N]^-$ [7,13], $[(SPMe_2)(OPPh_2)N]^-$ [7,13], $[(OPPh_2)(SPPh_2)N]^-$ [7,10,13–20], $[(OPPh_2)(SePPh_2)N]^-$ [16,19,20], $[(SPPh_2)(SePPh_2)N]^-$ [21], $[(SPPh_2)\{OP(OEt)_2\}N]^-$ [11,22], $[(OPPh_2)\{SP(OEt)_2\}N]^-$ [22] and $[\{OP(OPh)_2\}\{SP(OPh)_2\}N]^-$ [23].

Nickel(II) complexes of the type $Ni[(XPR_2)(XPR'_2)N]_2$, containing the same chalcogen atoms in the ligand unit, were reported, e.g. $Ni[(SPR_2)_2N]_2$ (R = Me [24,25], Ph [6,26]), $Ni[(SePPh_2)_2N]_2$ [27] and $Ni[(SPMe_2)(SPPh_2)N]_2$ [6]. All these complexes are monomeric and most of them contain a tetrahedral NiX_4 core. However, a square-planar NiS_4 core was found for $Ni[(SPMe_2)(SPPh_2)N]_2$, thus reflecting the capacity of such ligands to accommodate different tetracoordinated geometries required by the metal center [6]. No Ni(II) complexes containing mixed-chalcogen $[(XPR_2)(YPR'_2)N]^-$ have been reported so far, but for a palladium(II) derivative, $Pd[\{OP(OPh)_2\}\{SP(OPh)_2\}N]_2$ [23], an unusual S,N-coordination pattern was established.

On the other hand, a Cambridge Structure Database search for tetracordinated NiO_2S_2 core-containing complexes revealed that for all Ni(ligand-*O,S*)$_2$ compounds characterized so far by X-ray diffraction a square-planar coordination geometry was achieved regardless of

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[1] *Corresponding author.

[2] *Corresponding author.

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the size of chelate ring formed, i.e. five- [28–45] or six-membered [46–52].

Here we report on the synthesis and structural characterization of the first nickel(II) derivatives containing monothioimidodiphosphinato ligands, $Ni[(OPR'_2)(SPR_2)N]_2$.

2. Experimental

Sodium or potassium dichalcogenoimidodiphosphinates were prepared according to published methods: $K[(OPPh_2)(SPPh_2)N]$ [14], $K[(SPMe_2)(OPPh_2)N]$ and $Na[(OPMe_2)(SPPh_2)N]$ [13]. The IR spectra were recorded using KBr pellets on a Specord 75 IR Carl-Zeiss-Jena (DDR) instrument, in the range 4000–400 cm^{-1}.

Table 1
Crystallographic data for $Ni[(OPPh_2)(SPPh_2)N]_2$ (**1**) and $Ni[(OPPh_2)(SPMe_2)N]_2$ (**2**)

	1	**2**
Molecular formula	$C_{48}H_{40}O_2N_2P_4S_2Ni$	$C_{28}H_{32}O_2N_2P_4S_2Ni$
M	923.57	675.29
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Radiation	Mo Kα	Mo Kα
a (Å)	12.517(4)	11.360(2)
b (Å)	18.247(3)	16.613(3)
c (Å)	19.590(4)	8.737(3)
α (°)		94.06(2)
β (°)	100.73(2)	99.39(2)
γ (°)		82.56(1)
V (Å^3)	4396(1)	1611.1(6)
Z	4	2
Crystal size (mm)	0.40 × 0.35 × 0.30	0.38 × 0.38 × 0.35
$D_{calc.}$ (g cm^{-3})	1.39	1.39
F_{000}	1912.00	700.00
2θ Range (°)	2–50	2–50
μ(Mo Kα) (cm^{-1})	7.17	9.51
Max. and min. transmission factors	0.70–1.00	0.90–1.00
Temperature (°C)	23	23
Reflections measured	8413	6015
Reflections observed $[I_o < 3\sigma(I_o)]$, N_o	2259	1876
Parameters refined, N_p	272	212
Largest shift/e.s.d. in final cycle	0.001	0.001
Max., min. residual density peaks (e Å^{-3})	0.48, −0.37	0.42, −0.40
R [a]	0.0605	0.0601
R' [b]	0.0598	0.0475
Goodness-of-fit [c], S	1.80	1.38

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

2.1. Synthesis of $Ni[(OPPh_2)(SPPh_2)N]_2$ (**1**)

Clear methanol solutions containing $K[(OPPh_2)(SPPh_2)N]$ (0.471 g, 1.0 mmol, in 10 ml methanol) and $NiCl_2 \cdot 6H_2O$ (0.119 g, 0.5 mmol, in 10 ml methanol) were mixed and stirred for 2 h at room temperature (r.t.). The deep greenish-blue crystals of the title compound, which deposited in time, were filtered and recrystallized from a dichloromethane–methanol mixture. Yield: 0.32 g (69%). M.p. 159–161°C. IR (cm^{-1}): $\nu_{as}(P_2N)$ 1245vs, 1220vs; ν(PO) 1120s, 1045vs; ν(PS) 580m, 570vs.

2.2. Synthesis of $Ni[(OPPh_2)(SPMe_2)N]_2$ (**2**)

A reaction mixture obtained from stoichiometric amounts of $K[(OPPh_2)(SPMe_2)N]$ (0.694 g, 2.0 mmol) and $NiCl_2 \cdot 6H_2O$ (0.237 g, 1.0 mmol) in 20 ml of methanol was stirred at r.t. for 4 h. A greenish solid deposited and was filtered off. For purification it was dissolved in 20 ml chloroform and the insoluble KCl was removed by filtration. The title compound was obtained as dark blue crystals by slow diffusion using a 1:5 chloroform–n-hexane (v/v) solvent mixture. Yield: 0.49 g (73%). M.p. 164°C. IR (cm^{-1}): $\nu_{as}(P_2N)$ 1185vs,br; ν(PO) 1120s; ν(PS) 570m.

2.3. Synthesis of $Ni[(OPMe_2)(SPPh_2)N]_2$ (**3**)

A stoichiometric amount of $Na[(OPMe_2)(SPPh_2)N]$ (0.785 g, 2.37 mmol) was added to a solution of $NiCl_2 \cdot 6H_2O$ (0.282 g, 1.19 mmol) in 20 ml of methanol. The reaction mixture was stirred for 2 h at r.t. The resulting green solid was filtered off and then dissolved in 20 ml chloroform. The insoluble KCl was removed by filtration and the clear filtrate was evaporated. The title compound was isolated as light green crystals. Yield: 0.48 g (60%). M.p. 186–188°C. IR (cm^{-1}): $\nu_{as}(P_2N)$ 1175vs,br; ν(PO) 1110s; ν(PS) 615m, 585m.

2.4. Crystallographic structure determination

Details of the data collections and refinements are summarized in Table 1. Blue block crystals of $Ni[(OPPh_2)(SPPh_2)N]_2$ (**1**) and $Ni[(OPPh_2)(SPMe_2)N]_2$ (**2**), were mounted on glass fibers and sealed with epoxy glue. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation, operating at 50 kV and 35 mA. 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 $P2_1/c$ (No. 14) and $P\bar{1}$ (no. 2) for **1** and **2**, respectively. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods [53]. Only the nickel, sulfur, and phosphorus atoms in **1** and all

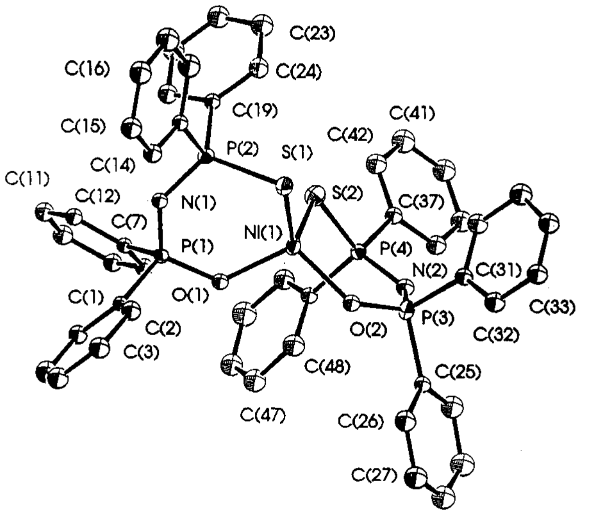

Fig. 1. An ORTEP plot of Ni[(OPPh$_2$)(SPPh$_2$)N]$_2$ (**1**) (the heavy atoms are drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity).

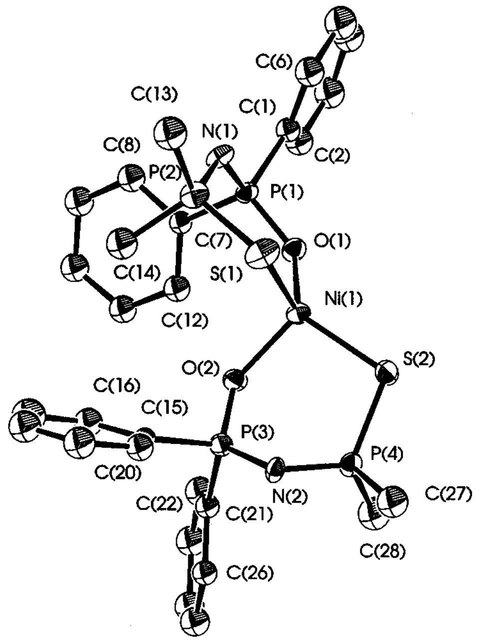

Fig. 2. An ORTEP plot of Ni[(OPPh$_2$)(SPMe$_2$)N]$_2$ (**2**) (the heavy atoms are drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity).

non-hydrogen atoms except carbon in **2** were treated anisotropically. The hydrogen atoms were included in their idealized positions with C–H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. Refinements were made by full-matrix least-squares using the TEXSAN [54] crystallographic package of the Molecular Structure Corp. Neutral-atom scattering factors were taken from Cromer and Waber [55]. Anomalous dispersion effects were included in F_c [56]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [57].

3. Results and discussion

The title compounds were obtained as crystalline solids by reacting NiCl$_2$·6H$_2$O with the alkaline salt of the appropriate monothioimidodiphosphinic acid, in methanol, according to Eq. (1):

$$\mathrm{NiCl_2{\cdot}6H_2O + 2M[(OPR'_2)(SPR_2)N]}$$
$$\rightarrow \mathrm{Ni[(OPR'_2)(SPR_2)N]_2 + 2MCl + 6H_2O} \quad (1)$$

The strong infrared absorptions observed for all these nickel(II) complexes in the regions 1250–1170, 1120–1040 and 620–570 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 acids and their alkaline salts, thus suggesting bidentate coordination of the ligand unit through both chalcogen atoms.

The solid-state structures of Ni[(OPPh$_2$)(SPR$_2$)N]$_2$ [R = Ph (**1**), Me (**2**)] were determined by single-crystal X-ray diffraction. For both compounds the crystal contains discrete monomeric molecules separated by normal van der Waals distances. The ORTEP plots of the molecular structures of **1** and **2** are displayed in Figs. 1 and 2. Important bond lengths and angles are listed in Table 2.

The molecular structure of **1** and **2** complexes are very similar. In a molecular unit both monothioimidodiphosphinato ligands are coordinated to a metal center in a monometallic biconnective pattern through both chalcogen atoms. The result is a spiro-bicyclic system with a tetrahedral NiO$_2$S$_2$ core, which is preserved in solution too as reflected by paramagnetic behavior which prevents the NMR study of these complexes. This contrasts with the square-planar NiO$_2$S$_2$ core observed for bis(monothio-β-diketonato)nickel(II) [28–34] and related complexes [37–43].

The P–S [range 2.012(5)–2.026(5) Å] and the P–N bonds [range 1.57(1)–1.610(9) Å] are equal, within the experimental errors, and their lengths are intermediate between single and double phosphorus–sulfur and phosphorus–nitrogen bonds, cf. the free acids (O=PPh$_2$)(S=PPh$_2$)NH [17]: P=S 1.935(2), (S)P–N 1.694(4), (O)P–N 1.668(5), P=O 1.491(4) Å; (O=PPh$_2$)(S=PMe$_2$)NH [13]: P=S 1.944(3), (S)P–N 1.681(7), (O)P–N 1.662(7), P=O 1.480(5) Å; and [(Me$_3$Si)$_2$N–P(=NBu^t)S]$_2$ [58]: P=N 1.529(2), P–N 1.662(2) Å. The P–O bond distances have also intermediate values between single and double phosphorus–oxygen bonds (cf. Ph$_2$P(=O)OH [59]: P–O 1.526(6), P=O 1.486(6) Å), but some small differences are observed probably due to the nature of the organic groups attached to the corresponding phosphorus atoms, i.e.

Table 2
Important bond lengths (Å) and angles (°) for $Ni[(OPPh_2)(SPPh_2)N]_2$ (**1**) and $Ni[(OPPh_2)(SPMe_2)N]_2$ (**2**)

	1	**2**		**1**	**2**
Ni(1)–O(1)	1.950(8)	1.959(7)	Ni(1)–O(2)	1.956(7)	1.950(7)
Ni(1)–S(1)	2.306(4)	2.306(4)	Ni(1)–S(2)	2.286(4)	2.305(4)
P(1)–O(1)	1.561(8)	1.521(7)	P(3)–O(2)	1.588(8)	1.530(7)
P(1)–N(1)	1.57(1)	1.610(9)	P(3)–N(2)	1.57(1)	1.589(9)
P(2)–N(1)	1.59(1)	1.589(9)	P(4)–N(2)	1.59(1)	1.599(9)
P(2)–S(1)	2.016(5)	2.023(5)	P(4)–S(2)	2.012(5)	2.026(5)
O(1)···S(1)	3.388(8)	3.363(8)	O(2)···S(2)	3.425(8)	3.377(8)
O(1)–Ni(1)–S(1)	105.2(2)	103.8(2)	O(2)–Ni(1)–S(2)	107.4(3)	104.7(2)
O(1)–Ni(1)–S(2)	112.5(3)	127.0(2)	O(2)–Ni(1)–S(1)	116.1(3)	112.2(3)
O(1)–Ni(1)–O(2)	107.7(3)	101.8(3)	S(1)–Ni(1)–S(2)	107.9(2)	107.2(1)
Ni(1)–O(1)–P(1)	126.5(5)	129.3(4)	Ni(1)–O(2)–P(3)	125.6(5)	125.4(4)
Ni(1)–S(1)–P(2)	98.9(2)	100.0(2)	Ni(1)–S(2)–P(4)	101.2(2)	102.5(2)
O(1)–P(1)–N(1)	117.8(5)	116.0(5)	O(2)–P(3)–N(2)	119.1(5)	117.3(4)
P(1)–N(1)–P(2)	133.7(6)	123.9(6)	P(3)–N(2)–P(4)	130.5(7)	122.6(5)
S(1)–P(2)–N(1)	116.7(4)	114.9(4)	S(2)–P(4)–N(2)	117.4(4)	116.5(4)

P–O = 1.561(8) and 1.588(8) Å for **1** and 1.521(7) and 1.530(7) Å for **2**, respectively.

The Ni–S [range 2.286(4)–2.306(4) Å] and Ni–O [range 1.950(7)–1.959(7) Å] bond distances are similar in both 1 and 2, within the experimental errors. The nickel-sulfur bond distances are very close to those found in tetrahedral $Ni[(SPMe_2)_2N]_2$ (av. 2.282 Å), $Ni[(SPPr^i_2)_2N]_2$ (av. 2.284 Å) or $Ni[(SPPh_2)_2N]_2$ (av. 2.299 Å), but longer than the predicted covalent Ni–S distance in a tetrahedral environment [$\Sigma_{cov}(Ni_{TD},S)$, 2.23 Å], as are the nickel–oxygen bond distances [$\Sigma_{cov}(Ni_{TD},O)$ 1.94 Å] [60,61].

The tetrahedral NiO_2S_2 cores are slightly distorted, the bond angles at the Ni center range from 105.2(2) to 116.1(3)° in **1**, and 101.8(3) to 127.0(2)° in **2**, respectively. The higher distortion of **2** from the ideal tetrahedral bond angle of 109.5° is also reflected by the dihedral angles between the S(1)Ni(1)O(1) and S(2)Ni(1)O(2) planes: 79.9° in **2** and 85.3° in **1**. The high flexibility of the OPNPS skeleton, which allows an O···S ligand bite larger [3.388(8), 3.425(8) Å in **1**, and 3.363(8), 3.377(8) Å in **2**] than in the related monothio-β-diketonato ligands (e.g. $Ni[(OCMe)(SCMe)CH]_2$ [30]: av. O···S, 3.00 Å), seems to be one contributing factor to the achievement of the tetrahedral coordination around the nickel center.

The six-membered $NiSOP_2N$ rings are not planar and their conformation, as reflected by the torsion angles, is also consistent with a high flexibility of the OPNPS systems. Thus, for **1** the two chelate rings display twisted chair and twisted boat conformations, with P(1)/S(1) and P(3)/S(2) atoms, respectively, in the apices. For **2** the chelate rings also display twisted chair and twisted boat conformations, but in this case the Ni(1)/N(1) and Ni(1)/N(2) atoms are placed in the apices.

4. Supplementary material

A complete listing of the crystal data is provided in the Supporting Information which contains tables giving final fractional coordinates and B_{eq} for non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates and B_{eq} for hydrogen atoms, all bond lengths and angles and ORTEP drawings for $Ni[(OPPh_2)(SPPh_2)N]_2$ and $Ni[(OPPh_2)(SPMe_2)N]_2$ (17 pages). Structure-factor tables are available from the authors (J.E.D. and A.S.) upon request.

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