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The influence of the intramolecular hydrogen bond on the 1,3-*N*,*S*- and 1,5-*O*,*S*-coordination of *N*-phosphoryl-*N*′-(R)-thioureas with Ni(II) and Pd(II)

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Reaction of the potassium salts of *N*-phosphorylated thioureas of common formula R^1–N(H)–C(S)–N(H)–P(O)(O*i*Pr)$_2$ (**HA**) with Ni^{II} and Pd^{II} cations leads to [M**A**$_2$] chelate complexes (M = Ni^{II}, R^1 = *p*-MeOC$_6$H$_4$, *p*-BrC$_6$H$_4$, *t*-Bu, *c*-Hex; M = Pd^{II}, R = *i*Pr). In both the Ni^{II} and Pd^{II} complexes, the metal center is found in a square-planar N_2S_2 environment formed by the C=S sulfur atoms and the P–N nitrogen atoms of two deprotonated ligands $\mathbf{A}^-$. The Pd^{II} atoms in [Pd**B**$_2$] complexes with deprotonated thioureas of common formula R^2–C(S)–N(H)–P(O)(O*i*Pr)$_2$ (**HB**) (R^2 = Et$_2$N, morpholine-*N*-yl) are coordinated in a square-planar fashion by the C=S sulfur atoms and the P=O oxygen atoms of two anionic ligands. Molecular structures of four complexes [M(**A**-*N*,*S*)$_2$] (M = Ni^{II}, R^1 = *p*-MeOC$_6$H$_4$, *p*-BrC$_6$H$_4$, *t*-Bu; M = Pd^{II}, R^1 = *i*Pr) and the palladium(II) 1,5-*O*,*S*-chelate of formula [Pd(**B**-*O*,*S*)$_2$] (R^2 = morpholine-*N*-yl) were elucidated by X-ray diffraction.

Introduction

The coordination chemistry of polyfunctional ligands, capable to realize different coordination modes with metal cations[1] is of interest for synthesis of new selective complexing agents and analytical reagents. The reasons allowing such ligands to bind metal ions in the various specific ways are intimately connected with such fundamental questions of chemistry as the nature of chemical bonding and the isomerism of coordination compounds, as well as the influence of the ligand structure on regio- and stereoselectivity of bond formation.

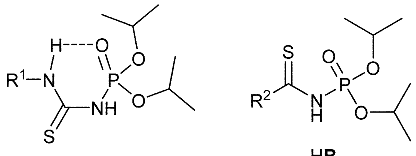
N-(Thio)phosphinyl(thio)ureas of the common formula RR′N–C(X)–N(H)–P(Y)(R″)$_2$ (R, R′ = alkyl, aryl, H; R″ = aryl, O-alkyl, O-aryl, N-alkyl$_2$; X, Y = O, S), as a rule, form 1,5-*X*,*Y*-chelates with metal cations.[2–4] Recently, we reported, that in the square-planar complexes of *N*-phosphrylthioureas [M{PhN(H)–C(*S*)–*N*–P(O)(O*i*Pr)$_2$}$_2$], where M = Ni^{II} or Pd^{II},[5] and [Cu{RN(H)–C(*S*)–*N*–P(O)(O*i*Pr)$_2$}$_2$] (R = Ph, *c*-Hex),[6] 1,3-*N*,*S*-coordination of the ligand is realized.

We have proposed two reasons for the higher stability of the [M(**L**-1,3-*N*,*S*)$_2$] relative to [M(**L**-1,5-*O*,*S*)$_2$] coordination mode. These include (i) a higher crystal field stabilization energies (CFSE) for the low-spin d^8 [M{PhN(H)–C(S)–NP(O)(O*i*Pr)$_2$-*N*,*S*}$_2$] complexes due to a stronger ligand field generated by of the amide N^- atom in comparison with the P=O oxygen atom and (ii) the formation of intramolecular NH···O=P hydrogen bonds in the complexes. DFT calculations have shown, that each intramolecular hydrogen bond contributes around 20–25 kJ mol^{-1}.[5,6] The substantial contribution of the hydrogen bonds towards the stability of the resulting complexes makes these an essential factor for 1,3-*N*,*S*-coordination of *N*-phosphorylthioureas.

To verify the assumptions made above, we have carried out the comparative study on the complexes of the Ni^{II} and Pd^{II} ions with *N*-phosphorylthioureas (Scheme 1), containing secondary (**HA**) and tertiary (**HB**) nitrogen at the *N*-thioacylamidophosphate moiety C(S)–N(H)–P(O)(O*i*Pr)$_2$ (**NAAP**).

Results and discussion

Nickel(II) chelates with the thioureas **HA**$^{1-4}$ of the common formula [Ni(**A**)$_2$] were prepared as follows. The ligands were



HA **HB**

R^1 = *p*-MeOC$_6$H$_4$: **HA**^{1}
R^1 = *p*-BrOC$_6$H$_4$: **HA**^{2}
R^1 = *t*Bu: **HA**^{3}
R^1 = *c*-Hex: **HA**^{4}
R^1 = *i*Pr: **HA**^{5}

R^2 = Et$_2$N: **HB**^{1}
R^2 = *N*-Morph: **HB**^{2}

Scheme 1 Ligands of type HA and HB.

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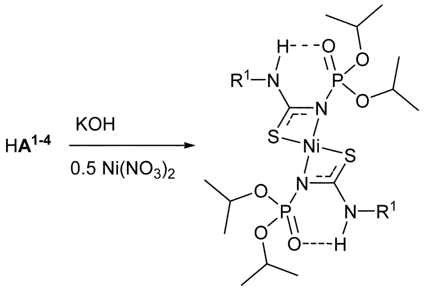


Scheme 2 Preparation of complexes [Ni($\mathbf{A}$-N,S)$_2$].

converted into the potassium salts $\mathbf{KA^{1-4}}$ which were reacted with Ni(NO$_3$)$_2$ in aqueous EtOH (Scheme 2).

The compounds obtained were crystalline solids that are soluble in most polar solvents. The molecular structures of these compounds were investigated by electron impact mass-spectrometry (EI-MS), IR, ^{1}H, ^{31}P{^{1}H} NMR spectroscopy and by elemental analysis. The Ni^{II} atom in these complexes was found in a square-planar N$_2$S$_2$ environment formed by the nitrogen and sulfur atoms of the N–P and C═S groups.

Application of the same procedure using the thioureas $\mathbf{HB^1}$ and $\mathbf{HB^2}$ did not result in isolation of individual products. According to the ^{1}H NMR spectra a complicated mixture of complex species formed which was difficult to analyze.

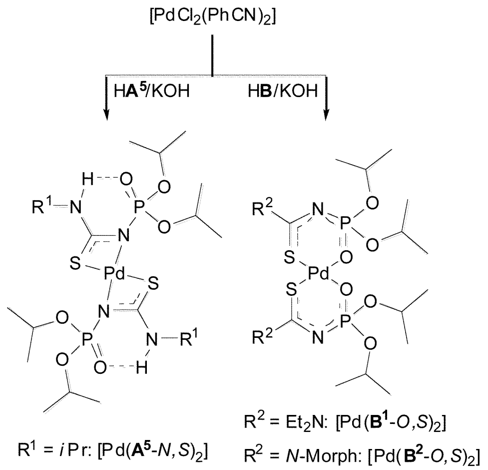
Earlier studies on the 1,5-S,S'-complexes of the Ni^{II} ion with N-thiophosphorylated thiourea PhN(H)–C(S)–N(H)–P(S)(OiPr)$_2$[7a] in CD$_2$Cl$_2$ solution have shown that a multi-component equilibrium between complex species with a tetrahedral or square-planar coordination geometry around the tetracoordinated metal ion. In these cases the product mixture can become even more complicated due to the formation of the five- and six-coordinated Ni^{II} species which might exhibit a 1,5-O,S- or 1,3-N,S-type of coordination.

Palladium(II) complexes were prepared from ligands $\mathbf{HA^5}$, $\mathbf{HB^1}$ and $\mathbf{HB^2}$ by conversion of the ligands into their potassium salts and subsequent reaction with [PdCl$_2$(PhCN)$_2$] in an aqueous EtOH/CH$_3$CN solution (Scheme 3).

The complexes obtained are crystalline solids that are soluble in most polar solvents and insoluble in n-hexane. They were investigated by electron impact mass-spectrometry (EI-MS), IR, ^{1}H, ^{31}P{^{1}H} NMR spectroscopy and by elemental analysis. A comparative analysis of the spectral characteristics indicated, that the Pd^{II} atom in [Pd($\mathbf{A^5}$)$_2$] is coordinated in a square-planar N$_2$S$_2$ environment whereas the [Pd($\mathbf{B}$)$_2$] complexes contain two anionic ligands bound in the 1,5-O,S-coordination mode. Apparently, the inability of coordinated ligands $\mathbf{B}^-$ to form intramolecular hydrogen-bonds leads to a destabilization of the [M($\mathbf{B}$-N,S)$_2$] complexes and the formation of complexes containing the ligand in the 1,5-O,S-coordination mode.

The molecular structures of four $trans$-1,3-N,S-chelates [Ni($\mathbf{A^1}$)$_2$], [Ni($\mathbf{A^2}$)$_2$], [Ni($\mathbf{A^3}$)$_2$], [Pd($\mathbf{A^5}$)$_2$] and one cis-1,5-O,S-chelate complex [Pd($\mathbf{B^2}$)$_2$] were determined by single-crystal X-ray diffraction analysis confirming the conclusions derived form the spectroscopic analysis.

The coordination mode of the ligands can be reliably followed by the IR spectroscopy (Table 1). The absorption bands of the P═O group of the anionic ligand $\mathbf{A}^-$ in complexes [Ni($\mathbf{A^{1-4}}$-N,S)$_2$] and [Pd($\mathbf{A^5}$-N,S)$_2$] are shifted by 4–32 cm^{-1} to lower wave numbers in comparison to the parent ligand. In contrast to this, involvement of the P═O oxygen atoms in the coordination to the Pd^{II} ion in complexes [Pd-($\mathbf{B}$-O,S)$_2$] results in a decrease of the wave number for the P═O stretching mode by 80 to 136 cm^{-1}. This shift compares well with the data obtained for 1,5-O,S-chelates of the Zn^{II},[7b] and Co^{II} [5,8] ions with **NAAP** ligands.



Scheme 3 Synthesis of palladium(II) complexes with ligands $\mathbf{HA^5}$, $\mathbf{HB^{1,2}}$.

The N–H absorption bands in the 1,3-N,S-chelates of Ni^{II} and Pd^{II} are observed in the range of ν 3120–3192 cm^{-1} which is the characteristic range for amide protons participating in hydrogen bonds. The IR spectra of complexes [Pd($\mathbf{B}$-O,S)$_2$] exhibit no absorption bands in this region.

Table 1 Comparison of IR and ^{31}P{^{1}H} spectroscopy data for 1,5-O,S- and 1,3-N,S-chelates of N-phosphorylthioureas

	$\Delta\nu$(PO)[c]	ν(NH)	$\Delta\delta_P$[c]	Ref.
$\mathbf{HA^1}$		3120, 3272		7b
[Ni($\mathbf{A^1}$)$_2$][a]	4	3160	9.11	
[Zn($\mathbf{A^1}$)$_2$]	108	3296	13.40	7b
$\mathbf{HA^2}$		3160, 3248		7b
[Ni($\mathbf{A^2}$)$_2$][a]	32	3120	7.62	
[Zn($\mathbf{A^2}$)$_2$]	100	3304	12.00	7b
$\mathbf{HA^3}$		3128, 3288		7b
[Ni($\mathbf{A^3}$)$_2$][a]	20	3184	8.43	
[Zn($\mathbf{A^3}$)$_2$]	92–128	3328	12.10	7b
$\mathbf{HA^4}$		3160, 3280		7b
[Ni($\mathbf{A^4}$)$_2$][a]	12	3192	7.51	
[Zn($\mathbf{A^4}$)$_2$]	88	3312	11.90	7b
$\mathbf{HA^5}$		3144, 3272		7b
[Pd($\mathbf{A^5}$)$_2$][a]	4	3208	7.84	
[Zn($\mathbf{A^5}$)$_2$]	80–112		9.6	7b
$\mathbf{HB^1}$		3128		7b
[Pd($\mathbf{B^1}$)$_2$][a]	100		13.26	
[Zn($\mathbf{B^1}$)$_2$]	105–136		9.6	7b
$\mathbf{HB^2}$		3128		7b
[Pd($\mathbf{B^2}$)$_2$][a]	81		13.69	
[Zn($\mathbf{B^2}$)$_2$]	116–132		10.2	7b
$\mathbf{HL}$[b]		3096, 3300		5
[Ni($\mathbf{L}$)$_2$]	14	3152	7.01	5
[Pd($\mathbf{L}$)$_2$]	10	3160	7.99	5
[Zn($\mathbf{L}$)$_2$]	100–114	3312	11.6	7b

[a] This work. [b] **HL** = PhN(H)–C(S)–N(H)–P(O)(OiPr)$_2$. [c] Difference between values for the free and coordinated ligand.

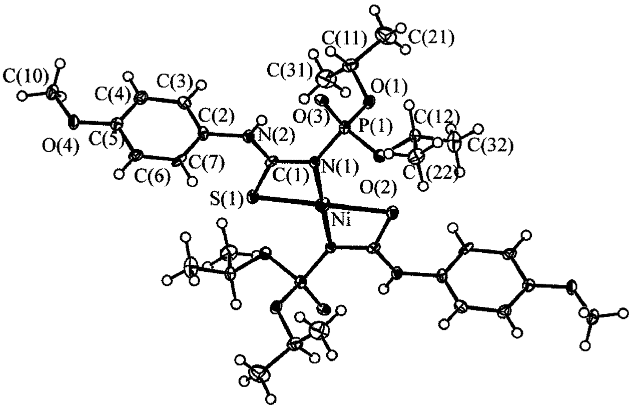


Fig. 1 Molecular structure of [Ni($\mathbf{A}^1$)$_2$]. Thermal ellipsoids are drawn at 50% probability.

Only one NH-proton signal was observed in the ^{1}H NMR spectra of complexes [Ni($\mathbf{A}^{1-4}$-*N*,*S*)$_2$] and [Pd($\mathbf{A}^5$-*N*,*S*)$_2$]. For the complexes of the thioureas H$\mathbf{A}^{3-5}$, containing alkyl substituents at the nitrogen atom, the amide proton resonance was observed in the range δ 8.47–8.55 ppm, while in the case of thioureas H$\mathbf{A}^1$ and H$\mathbf{A}^2$ the influence of the phenyl group in combination with its deshielding effects results in a shift of this signal to the δ 10.30–10.55 ppm range. In the ^{31}P{^{1}H} spectra a singlet signal with a chemical shift characteristic for the amidophosphate environment of the phosphorus nuclei (Table 1) was observed. These signals are low-field shifted in comparison to the corresponding resonance of the parent phosphorylated thiourea. As can been seen in Table 1, the ^{31}P{^{1}H} resonance in the 1,5-*O*,*S*-chelates is always observed at higher field than for the 1,3-*N*,*S*-analogues.

Crystals of [Ni($\mathbf{A}^{1-3}$-*N*,*S*)$_2$], and [Pd($\mathbf{A}^5$-*N*,*S*)$_2$] and [Pd($\mathbf{B}^2$-*N*,*O*)$_2$] were obtained by slow evaporation of the solvent from dichloromethane–*n*-hexane solutions of the complexes.

The complexes [Ni($\mathbf{A}^{1,2}$)$_2$] (Fig. 1 and 2) are built in a centrosymmetric manner. The asymmetric unit of [Ni($\mathbf{A}^3$)$_2$] contains two independent molecules which also possess a center of symmetry (Fig. 3). Selected bond lengths and bond and torsion angles for these complexes are summarized in Table 2.

The Ni$^{\text{II}}$ and Pd$^{\text{II}}$ ions in [Ni($\mathbf{A}^{1-3}$-*N*,*S*)$_2$] and [Pd($\mathbf{A}^5$-*N*,*S*)$_2$] (Fig. 4) chelates are coordinated in a square-planar fashion with the ligands arranged in *trans*-configuration. The four-membered M–S–C–N metallocycles are flat. The values of the intracyclic S–Ni–N angles in the four-membered rings fall in the range of 70–75°. Inspection of the C–S and P–N bond lengths indicates, that these bonds are best described as single bonds, while the P=O separation indicates the presence of a double bond.[9]

In all investigated compounds the RN(H) protons are engaged in intramolecular hydrogen bonds of the RNH···O=P type (Table 3). Due to their formation, a flat *syn*,*syn*-conformation of the N–C–N–P–O unit is favored.

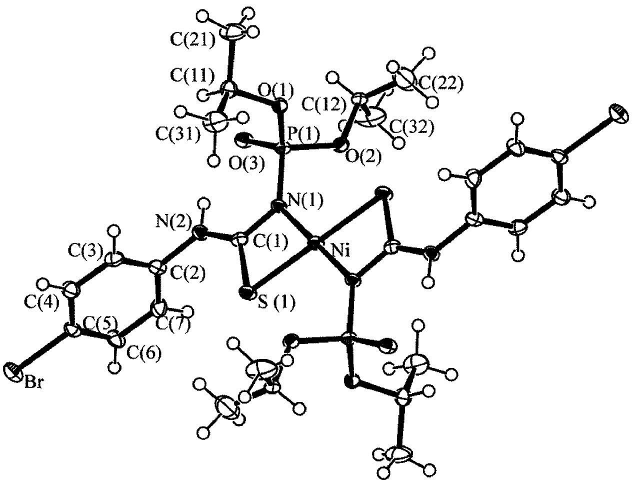


Fig. 2 Molecular structure of [Ni($\mathbf{A}^2$)$_2$]. Thermal ellipsoids are drawn at 50% probability.

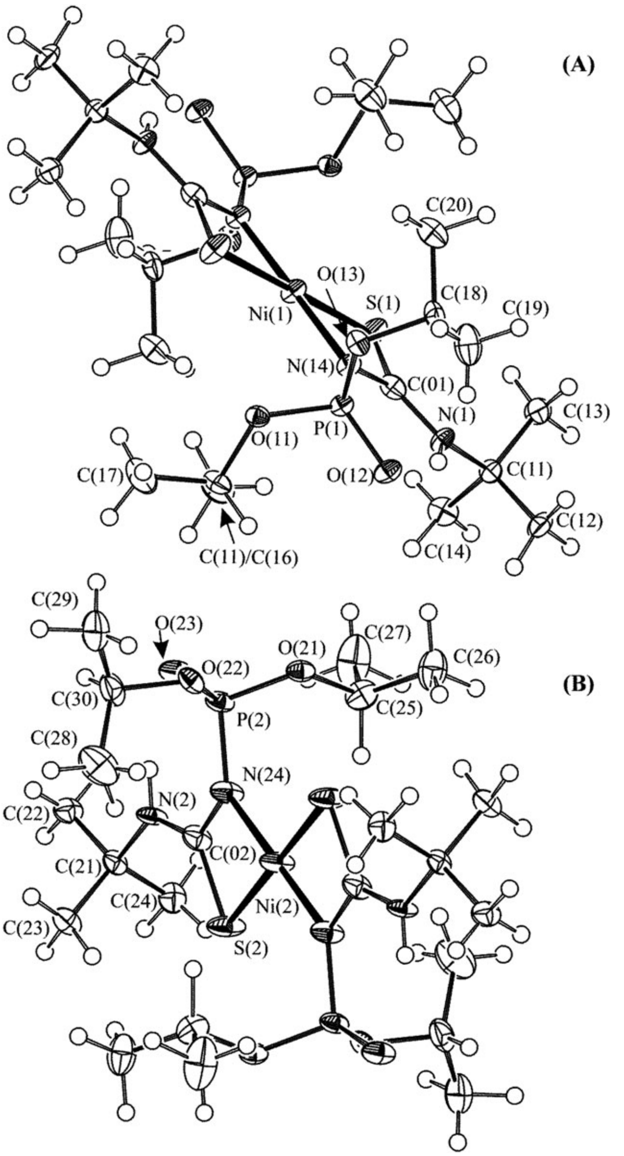


Fig. 3 Crystal structure of two independent centrosymmetrical molecules (A) and (B) in a crystal of complex [Ni($\mathbf{A}^3$)$_2$]. Thermal ellipsoids are drawn at 50% probability.

Table 2 Selected bond lengths (Å), and bond angles (°) for four-membered cycles M–S–C–N in complexes $[\mathrm{Ni}(\mathbf{A}^{1-3}\text{-}N,S)_2]$ and $[\mathrm{Pd}(\mathbf{A}^{5}\text{-}N,S)_2]$, and six-membered M–S–C–N–P–O cycles in $[\mathrm{Pd}(\mathbf{B}^{2}\text{-}O,S)_2]$

	$[\mathrm{Ni}(\mathbf{A}^1)_2]$	$[\mathrm{Ni}(\mathbf{A}^2)_2]$	$[\mathrm{Ni}(\mathbf{A}^3)_2]^a$ (A)	$[\mathrm{Ni}(\mathbf{A}^3)_2]^a$ (B)	$[\mathrm{Ni}(\mathbf{L})_2]^{b,5}$	$[\mathrm{Pd}(\mathbf{A}^5)_2]$	$[\mathrm{Pd}(\mathbf{B}^2)_2]$ ^{a}(A)	$[\mathrm{Pd}(\mathbf{B}^2)_2]$ ^{a}(B)	$[\mathrm{Pd}(\mathbf{L})_2]^5$
M–S	2.2440(11)	2.2277(9)	2.2130(9)	2.2192(13)	2.2209(13), 2.2203(13)	2.3279(11), 2.3580(11)	2.2624(14), 2.2497(14)	2.2574(14), 2.2518(14)	2.3323(8), 2.3306(8)
M–N	1.912(3)	1.909(2)	1.896(2)	1.895(3)	1.907(3), 1.906(3)	2.034(3), 2.030(3)			2.0284(15), 2.0307(15)
M–O							2.060(3), 2.074(3)	2.074(3), 2.060(3)	
C–S	1.713(4)	1.725(3)	1.741(3)	1.716(3)	1.732(4), 1.737(4)	1.738(4), 1.739(4)	1.757(5), 1.767(5)	1.751(5), 1.768(5)	1.7382(19), 1.7347(18)
C–N	1.362(5)	1.342(4)	1.354(4)	1.353(4)	1.332(4), 1.342(4)	1.342(5), 1.347(5)	1.311(6), 1.304(6)	1.304(6), 1.305(6)	1.330(2), 1.332(2)
C–N (exocyclic)	1.335(5)	1.432(4)	1.313(4)	1.329(4)	1.337(4), 1.329(4)	1.320(5), 1.321(5)	1.356(6), 1.344(6)	1.351(6), 1.356(6)	1.338(2), 1.337(2)
P–N	1.646(3)	1.653(2)	1.661(2)	1.645(3)	1.655(3), 1.647(3)	1.650(3), 1.648(3)	1.592(4), 1.596(4)	1.594(4), 1.587(4)	1.6548(16), 1.6459(16)
P═O	1.475(3)	1.482(2)	1.460(2)	1.476(2)	1.471(2), 1.471(2)	1.475(3), 1.472(3)	1.503(4), 1.511(4)	1.491(4), 1.509(4)	1.4664(14), 1.4713(14)
N–C–S (endocyclic)	110.6(3)	110.1(2)	108.3(2)	107.9(2)	109.64(13), 109.78(13)	109.4(3), 110.2(3)	126.8(4), 127.0(4)	126.9(4), 127.4(4)	109.1(3), 108.5(3)
S–M–X (endocyclic), (X = N, O)	74.74(10)	74.74(8)	75.20(8)	74.04(9)	74.36(9), 74.50(9)	70.45(9), 70.33(9)	93.48(10), 95.14(10)	96.75(10), 93.28(10)	70.16(5), 70.18(5)

[a] The data for two independent molecules (A) and (B). [b] H**L** = PhN(H)–C(S)–N(H)–P(O)(O*i*Pr)$_2$.

Complex $[\mathrm{Pd}(\mathbf{B}^2)_2]$ is a spirocyclic bis-chelate (Fig. 5) with a *cis*-square-planar arrangement of the ligands around the $\mathrm{Pd}^{\mathrm{II}}$ ion. The deprotonated thiourea ligands are coordinated by the oxygen atoms of the phosphoryl groups and the thiocarbonyl sulfur atoms.

The asymmetric unit of $[\mathrm{Pd}(\mathbf{B}^2)_2]$ contains two independent molecules (A) and (B) differs by the mutual arrangement of the morpholine substituents.

All of the morpholine cycles are found in quite similar chair conformations. The molecule (A) (Fig. 5) has the "parallel" orientation of the two morpholine moieties, deflected to the same side of the $\mathrm{PdO_2S_2}$ plane. The morpholine rings in the molecule (B) are in *anti*-orientation about the $\mathrm{PdO_2S_2}$ plane.

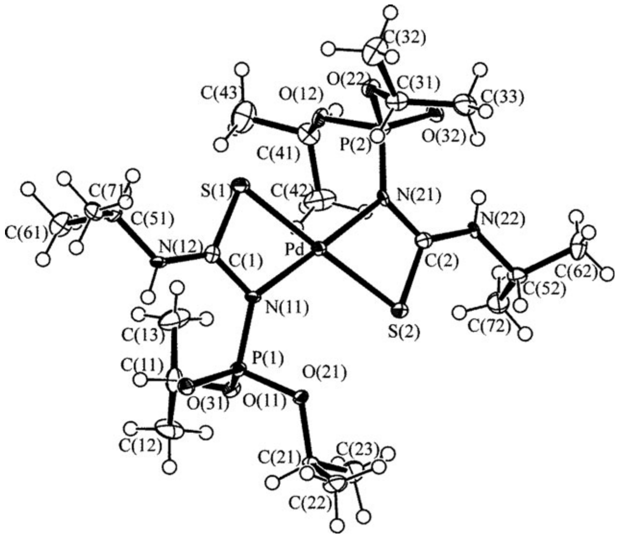


Fig. 4 Crystal structure of $[\mathrm{Pd}(\mathbf{A}^5)_2]$. Thermal ellipsoids are drawn at 50% probability.

Table 3 Parameters of hydrogen bonds for $\mathrm{Ni}^{\mathrm{II}}$ and $\mathrm{Pd}^{\mathrm{II}}$ chelates [bond lengths (Å), and bond angles (°)]

	N–H···A	*d*(H···A)	*d*(N···A)	∠(NHA)
$[\mathrm{Ni}(\mathbf{A}^1)_2]$	N(2)–H(2)···O(3)	2.04	2.761(4)	138
$[\mathrm{Ni}(\mathbf{A}^2)_2]$	N(2)–H(2)···O(3)	2.04	2.742(3)	139
$[\mathrm{Ni}(\mathbf{A}^3)]_2$	N(1)···H(1)···O(12)	2.05	2.777(3)	139
	N(2)···H(2)···O23	2.05	2.780(4)	140
$[\mathrm{Pd}(\mathbf{A}^5)_2]$	N(12)–H(12N)···O(31)	2.17	2.849(4)	133
	N(22)–H(22N)···O(32)	2.07	2.769(5)	138

The six-membered metallocycles Pd–S–C–N–P–O adopt a half-chair conformation and show a similar geometry. Both of them have nearly planar S–C–N–P and Pd–S–C–N moieties.

The differences in the coordination of the ligands $\mathbf{A}^-$ and $\mathbf{B}^-$ is reflected in the observed bond lengths within the chelate

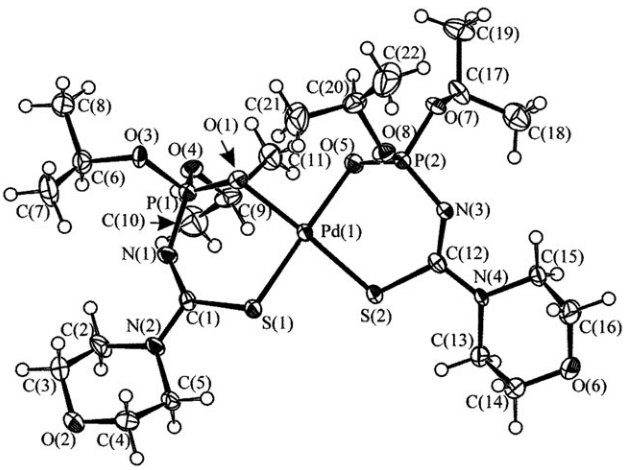


Fig. 5 Crystal structure of $[\mathrm{Pd}(\mathbf{B}^2)_2]$. The molecule (A) is shown. Thermal ellipsoids are drawn at 50% probability.

cycles. Predictably, coordination of the phosphoryl groups to palladium(II) leads to an appreciable reduction of the P–N bond lengths and an increase in length for the P═O bond (Table 2) in comparison with the 1,3-*N*,*S*-chelates. The C–S bonds in six-membered metallocycles are longer, and the C–N bonds are shorter, than in four-membered ones. These changes are a consequence of the negative charge delocalization in the S–C–N–P–O ring.[4a]

The 1,5-*O*,*S*-coordination mode leads to a considerably larger bite angle (O···S separation 3.15–3.19 Å) than the *N*,*S*-coordination (N···S separation 2.50–2.54 Å) which results in a smaller distortion of the square-planar environment at the central metal ion and the thiourea backbone geometry. A comparison of the S–C–N and S–Pd–X (X = N, O) angles is presented in Table 2.

Conclusions

The data presented allow to confirm, that at least for the investigated *N*-phosphorylthiourea ligands (Scheme 1) the formation of the intramolecular hydrogen bonds P═O···HNR is a necessary condition for the 1,3-*N*,*S*-isomer stabilization in a square-planar complexes of Ni^{II} and Pd^{II}. When H-bonding in the coordinated anionic ligands $(\mathbf{B^1})^-$ and $(\mathbf{B^2})^-$ is not possible the destabilization of Ni^{II} complexes and a change of the coordination mode in the Pd^{II} complexes occurs. Thus, the intramolecular hydrogen bonding realized outside the coordination sphere of the metal cation is the reason for the dramatic changes of such important parameters as bite angle and ligand's field strength.

Factors, influencing on the stabilization of the 1,3-*N*,*S*-isomers, essentially distinguish the **NAAP** ligands from their diphosphorus analogues—imidodiphosphinates $R_2P(X)$–N(H)–$P(Y)R'_2$.[10,11] The determining factor in the latter case is the presence of the acceptor substituents at the P═O group (X = O, Y = S, R = O-aryl). It is known, that for the Pd^{II} complexes with $(PhO)_2P(O)$–N(H)–$P(S)R'_2$ (R′ = OPh,[12] Ph,[13] *i*Pr[13]) the 1,3-*N*,*S*-coordination mode is realized. Similar ligands, containing the $Ph_2P(O)$ group, form 1,5-*O*,*S*-chelates both with the Ni^{II} and Pd^{II} ions.[14]

Experimental

General procedures

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^1H) and H_3PO_4 ($^{31}P\{^1H\}$). Electron ionisation mass spectra were measured on a TRACE MS Finnigan MAT instrument. The ionisation energy was 70 eV. The substance was injected directly into the ion source at 150 °C. Heating was carried out in a programmed mode from 35–200 °C at a rate of 35 °C min^{-1}. Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyser.

Syntheses

HA^1–HA^5 and $HB^{1,2}$. *N*-Diisopropoxyphosphorylthioureas were prepared according to the previously described methods.[5,7b]

$[Ni(A^{1-4})_2]$. A suspension of HA^{1-4} (1.730, 1.975, 1.480 or 1.610 g, respectively; 5 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.280 g, 5 mmol). An aqueous (20 mL) solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.815 g, 2.8 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 5 h and left overnight. The resulting complex was extracted with dichloromethane, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed *in vacuo*. A precipitate was isolated from dichloromethane by *n*-hexane.

$[Ni(A^1)_2]$. Yield (based on the ligand) 1.571 g (84%). Mp 171 °C. ^1H NMR ($CDCl_3$): δ 1.36 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, CH_3), 1.64 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, CH_3), 3.80 (s, 6 H, OCH_3), 4.66 (d sept, $^3J_{H,H} \approx {}^3J_{P,H}$ = 6.3 Hz, 4 H, OCH), 6.86–7.29 (m, 8 H, C_6H_4), 10.30 [s, 2 H, NHC(S)] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.2 ppm. IR: $\tilde{\nu}$ 992 (POC), 1240 (P═O), 1552 (SCN), 3160 (NH) cm^{-1}. EI-MS: *m*/*z* (%) 748 (24) $[M]^+$. $C_{28}H_{44}N_4O_8P_2S_2Ni$ (748.14): calc. C 44.87, H 5.92, N 7.48; found: C 44.81, H 5.86, N 7.39%.

$[Ni(A^2)_2]$. Yield (based on the ligand) 1.139 g (54%). Mp 175 °C. ^1H NMR ($CDCl_3$): δ 1.32 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, CH_3), 1.60 (d, $^3J_{H,H}$ = 6.3 Hz, 12 H, CH_3), 4.61 (d. sept, $^3J_{H,H} \approx {}^3J_{P,H}$ = 6.3 Hz, 4 H, OCH), 7.28–7.48 (m, 8 H, C_6H_4), 10.55 [s, 2 H, NHC(S)] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.8 ppm. IR: $\tilde{\nu}$ 1012 (POC), 1192 (P═O), 1548 (SCN), 3120 (NH) cm^{-1}. EI-MS: *m*/*z* (%) 844 (11) $[M]^+$. $C_{26}H_{38}Br_2N_4O_6P_2S_2Ni$ (843.94): calc. C 36.86, H 4.52, N 6.61; found: C 36.80, H 4.44, N 6.58%.

$[Ni(A^3)_2]$. Yield (based on the ligand) 1.004 g (62%). Mp 131 °C. ^1H NMR ($CDCl_3$): δ 1.26–1.49 (m, 24 H, CH_3), 1.61 (s, 18 H, CH_3, *t*Bu), 4.52–4.75 (m, 4 H, OCH), 8.47 [s, 2 H, NHC(S)] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.0 ppm. IR: $\tilde{\nu}$ 980, 1016 (POC), 1216 (P═O), 1564 (SCN), 3184 (NH) cm^{-1}. EI-MS: *m*/*z* (%) 649 (10) $[M]^+$. $C_{22}H_{48}N_4O_6P_2S_2Ni$ (648.18): calc. C 40.69, H 7.45, N 8.63; found: C 40.64, H 7.40, N 8.69%.

$[Ni(A^4)_2]$. Yield (based on the ligand) 0.963 g (55%). Mp 175 °C. ^1H NMR ($CDCl_3$): δ 1.37–2.03 (m, 44 H, CH_3 + *c*-C_6H_{11} (without CHN)), 3.46–3.74 (m, 2 H, CHN), 4.48–4.80 (m, 4 H, OCH), 8.47 [s, 2 H, NHC(S)] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.7 ppm. IR: $\tilde{\nu}$ 1000 (POC), 1208 (P═O), 1564 (SCN), 3192 (NH) cm^{-1}. EI-MS: *m*/*z* (%) 701 (2) $[M]^+$. $C_{26}H_{52}N_4O_6P_2S_2Ni$ (700.22): calc. C 44.52, H 7.47, N 7.99; found: C 44.16, H 7.24, N 7.59%.

$[Pd(A^5)_2]$ and $[Pd(B^{1,2})_2]$. A suspension of HA^5 or $HB^{1,2}$ (1.410, 1.480 or 1.550 g, respectively; 5 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.280 g, 5 mmol). An acetonitrile (20 mL) solution of $[PdCl_2(PhCN)_2]$ (1.072 g, 2.8 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for further 5 h and left overnight. The resulting complex was extracted with dichloromethane, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed *in vacuo*. A precipitate was isolated from dichloromethane by *n*-hexane.

[Pd(A^5)$_2$]. Yield (based on the ligand) 1.186 g (71%). Mp 116 °C. ^{1}H NMR ($CDCl_3$): δ 1.22 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH_3, *i*PrN), 1.35 (d, $^3J_{H,H}$ = 6.1 Hz, 12 H, CH_3, *i*PrO), 1.45 (d, $^3J_{H,H}$ = 6.1 Hz, 12 H, CH_3, *i*PrO), 4.01 (d sept, $^3J_{HCNH}$ = 8.4 Hz, $^3J_{H,H}$ = 6.6 Hz, 2 H, NCH), 4.59 (d sept, $^3J_{P,H}$ = 6.4 Hz, $^3J_{H,H}$ = 6.1 Hz, 4 H, OCH), 8.55 [d, $^3J_{HCNH}$ = 8.4 Hz, 2 H, NHC(S)] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 2.5 ppm. IR: $\tilde{\nu}$ 980 (POC), 1212 (P=O), 1560 (SCN), 3208 (NH) cm^{-1}. EI-MS: m/z (%) 669 (4) [M]$^+$. $C_{20}H_{44}N_4O_6P_2S_2Pd$ (668.12): calc. C 35.90, H 6.63, N 8.37; found: C 35.93, H 6.58, N 8.41%.

[Pd(B^1)$_2$]. Yield (based on the ligand) 0.818 g (47%). Mp 120 °C. ^{1}H NMR ($CDCl_3$): δ 1.02–1.26 (m, 12 H, CH_3, Et_2N), 1.29–1.39 (m, 24 H, CH_3, *i*PrO), 3.36–3.78 (m, 8 H, CH_2, Et_2N), 4.58-4.76 (m, 4 H, OCH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 9.4 ppm. IR: $\tilde{\nu}$ 1004 (POC), 1140 (P=O), 1528 (SCN) cm^{-1}. EI-MS: m/z (%) 696 (2) [M]$^+$. $C_{22}H_{48}N_4O_6P_2S_2Pd$ (696.15): calc. C 37.90, H 6.94, N 8.04; found: C 37.91, H 7.01, N 8.09%.

[Pd(B^2)$_2$]. Yield (based on the ligand) 0.941 g (52%). Mp 156 °C. ^{1}H NMR ($CDCl_3$): δ 1.33 (d, $^3J_{H,H}$ = 6.1 Hz, 12 H, CH_3), 1.34 (d, $^3J_{H,H}$ = 6.1 Hz, 12 H, CH_3), 3.62–3.95 (m, 16 H, CH_2), 4.67 (d sept, $^3J_{P,H}$ = 7.7 Hz, $^3J_{H,H}$ = 6.1 Hz, 4 H, OCH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 9.9 ppm. IR: $\tilde{\nu}$ 1006 (POC), 1155 (P=O), 1546 (SCN) cm^{-1}. EI-MS: m/z (%)-[M]$^+$ not observed. $C_{22}H_{44}N_4O_8P_2S_2Pd$ (724.11): calc. C 36.44, H 6.12, N 7.73; found: C 36.47, H 6.16, N 7.76%.

X-Ray crystallography

The data for [Ni(**A^1**)$_2$], [Ni(**A^2**)$_2$], [Ni(**A^3**)$_2$] and [Pd(**A^5**)$_2$], were collected at −173 °C using a KM4CCD diffractometer and graphite-monochromated Mo-Kα radiation generated from Diffraction X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated and scaled using the KUMA data reduction package.[15] The structure was solved by heavy atom and direct method using SHELX97[16] and refined by the full-matrix least-squares method on all F^2 data.[17] Non-hydrogen atoms were included in the refinement, with anisotropic displacement parameters: the atoms were positioned geometrically and refined as riding model.

X-Ray diffraction data for [Pd(**B^2**)$_2$] were collected on a Bruker AXS diffractometer equipped with a rotating anode generator and with Mo-Kα radiation. All raw data were corrected for absorption using SADABS.[18] The structure solutions were found with SHELXS,[19] and the refinement was carried out with SHELXL[17] using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions and were refined as rigid atoms.

[Ni(A^1)$_2$]. $C_{28}H_{44}N_4NiO_8P_2S_2$, M_r = 749.44 g mol^{-1}, violet prisms, monoclinic, space group $P2_1/n$, a = 12.194(2), b = 8.439(2), c = 16.951(3) Å, β = 91.55(3)°, V = 1743.7(6) Å^3, Z = 2, D_c = 1.427 g cm^{-3}, μ(Mo-Kα) = 0.819 mm^{-1}, reflections: 12 428 collected, 4044 unique, R_{int} = 0.0950, R_1(all) = 0.0610, wR_2(all) = 0.0996.

[Ni(A^2)$_2$]. $C_{26}H_{38}Br_2N_4NiO_6P_2S_2$, M_r = 847.20 g mol^{-1}, violet prisms, monoclinic, space group $P2_1/c$, a = 10.403(2), b = 8.304(2), c = 20.958(6) Å, β = 105.78(3)°, V = 1742.3(7) Å^3, Z = 2, D_c = 1.615 g cm^{-3}, μ(Mo-Kα) = 3.105 mm^{-1}, reflections: 20 389 collected, 6626 unique, R_{int} = 0.1080, R_1(all) = 0.0542, wR_2(all) = 0.0894.

[Ni(A^3)$_2$]. $C_{22}H_{48}N_4NiO_6P_2S_2$, M_r = 649.40 g mol^{-1}, violet prisms, triclinic, space group $P\bar{1}$ (no. 2), a = 9.273(2), b = 9.672(2), c = 21.274(4) Å, α = 97.75(3), β = 91.62(3)°, γ = 117.78(3)°, V = 1663.6(6) Å^3, Z = 2, D_c = 1.296 g cm^{-3}, μ(Mo-Kα) = 0.843 mm^{-1}, reflections: 13 466 collected, 7453 unique, R_{int} = 0.0603, R_1(all) = 0.0483, wR_2(all) = 0.1114.

[Pd(A^5)$_2$]. $C_{20}H_{44}N_4O_6P_2PdS_2$, M_r = 669.05 g mol^{-1}, yellow prisms, monoclinic, space group $P2_1/c$, a = 18.981, b = 9.764, c = 16.498 Å, β = 97.89(3)°, V = 3028.6(10) Å^3, Z = 4, D_c = 1.467 g cm^{-3}, μ(Mo-Kα) = 0.895 mm^{-1}, reflections: 19 817 collected, 6927 unique, R_{int} = 0.0648, R_1(all) = 0.0524, wR_2(all) = 0.0693.

[Pd(B^2)$_2$]. $C_{22}H_{44}N_4O_8P_2PdS_2$, M_r = 725.07 g mol^{-1}, red prisms, monoclinic, space group $P2_1/n$, a = 18.747(4), b = 17.566(4), c = 19.950(4) Å, β = 100.046(5)°, V = 6469(2) Å^3, Z = 8, D_c = 1.489 g cm^{-3}, μ(Mo-Kα) = 0.849 mm^{-1}, reflections: 51 115 collected, 11 411 unique, R_{int} = 0.0962, R_1(all) = 0.0555, wR_2(all) = 0.0959.

CCDC reference numbers 622814 ([Ni(**A^1**)$_2$]), 622815 ([Ni(**A^2**)$_2$]), 622816 ([Ni(**A^3**)$_2$]), 622817 ([Pd(**A^5**)$_2$]) and 635 626 ([Pd(**B^2**)$_2$]), respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702896b.

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