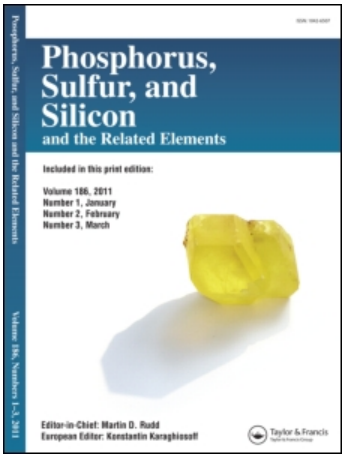

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Complexes of $[(i\text{PrO})_2\text{P(O)NHC(S)NHCH}_2]_2\text{CH}_2$ with Co(II), Ni(II), Zn(II), and Pd(II): Reaction of $[(i\text{PrO})_2\text{P(O)NHC(S)NHCH}_2]_2$ with KOH Leading to the Imidazolidine-2-Imine Derivative

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COMPLEXES OF $[(i\text{PrO})_2\text{P(O)NHC(S)NHCH}_2]_2\text{CH}_2$ WITH Co(II), Ni(II), Zn(II), AND Pd(II): REACTION OF $[(i\text{PrO})_2\text{P(O)NHC(S)NHCH}_2]_2$ WITH KOH LEADING TO THE IMIDAZOLIDINE-2-IMINE DERIVATIVE

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Reaction of O,O′-diisopropylphosphoric acid isothiocyanate $(iPrO)_2P(O)NCS$ with $NH_2(CH_2)_nNH_2$ (n = 3, 2) leads to the N-phosphorylated bis-thioureas $[(iPrO)_2C(S)NHP(O)NH]_2Z$ (Z = $-(CH_2)_3-$, H_2L^I; $-(CH_2)_2-$, H_2L^{II}). Reaction of the potassium salt of H_2L^I with Co(II) and Zn(II) in aqueous EtOH leads to complexes of formula $M_2(L\text{-}O,S)_2$. The metal cation in both complexes is coordinated by two deprotonated ligands through the sulfur atoms of the thiocarbonyl groups and the oxygen atoms of the phosphoryl groups. Reaction of K_2L^I with Ni(II) and Pd(II) in the same conditions leads to $M_2(L\text{-}N,S)_2$ complexes. In both compounds, 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 L^I. Reaction of H_2L^{II} with KOH leads to a product of heterocyclization, in which one of the thiourea fragments is retained. Compounds obtained were investigated by IR, UV-Vis, ^1H and ^{31}P NMR spectroscopy, and microanalysis.

Keywords Chelate; cobalt; complex; heterocycles; nickel; palladium; phosphorylthiourea; zinc

INTRODUCTION

The metal–organic architectures formed by *d*-metal cations and bifunctional chelators, e.g., bis-β-diketonates or bis-*N*-acylthioureas,[1] are of great interest due to their magnetic, gas storage, and catalytic properties. In this connection, the idea to use diamines armed by exocyclic chelating groups as ligands for building such structures seems rather attractive.

Combination of the spacer moiety and the exocyclic donor groups in one molecule is an effective way for design of selective complexing agents.[2–5] The derivatives of various crown-ethers bearing one or two acylamidophosphate fragments $-\text{C(X)NHP(Y)(OR)}_2$ (X, Y = O, S); their complexes with Co(II), Pd(II), Cu(I), and Cd(II) cations;[6] and selective binding of sodium cation[7] were reported earlier by our group.

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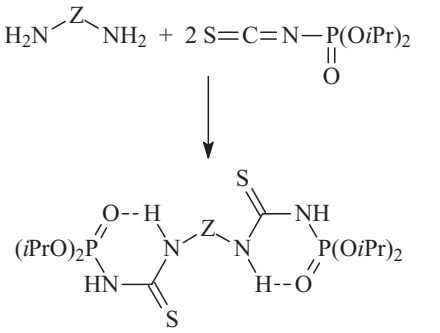
In this article, we present complexes of Co(II), Ni(II), Zn(II), and Pd(II) cations with $[(i\mathrm{PrO})_2\mathrm{C(S)NHP(O)NHCH_2]_2CH_2}$ (**H_2L^I**) and interaction of $[(i\mathrm{PrO})_2\mathrm{C(S)NHP(O)NHCH_2]_2}$ (**H_2L^{II}**) with KOH. Obtained compounds are doubtless of interest as building blocks for supramolecular compounds.

RESULTS AND DISCUSSION

Synthesis

Bis-thioureas **$H_2L^{I,II}$** were prepared by reaction of the corresponding diamine with $(i\mathrm{PrO})_2\mathrm{P(O)NCS}$ (Scheme 1). Complexes **$M_2L^I_2$** were prepared by the following procedure: the ligand was converted to the potassium salt, followed by interaction with $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $ZnCl_2$, or $Pd(PhCN)_2Cl_2$, respectively (Scheme 2). Reaction of **H_2L^{II}** with KOH leads to a product of heterocyclization—phosphorylated imidazolidine-2-imine derivative **HQ** (Scheme 3).



Z = —$(CH_2)_3$— (**H_2L^I**); —$(CH_2)_2$— (**H_2L^{II}**)

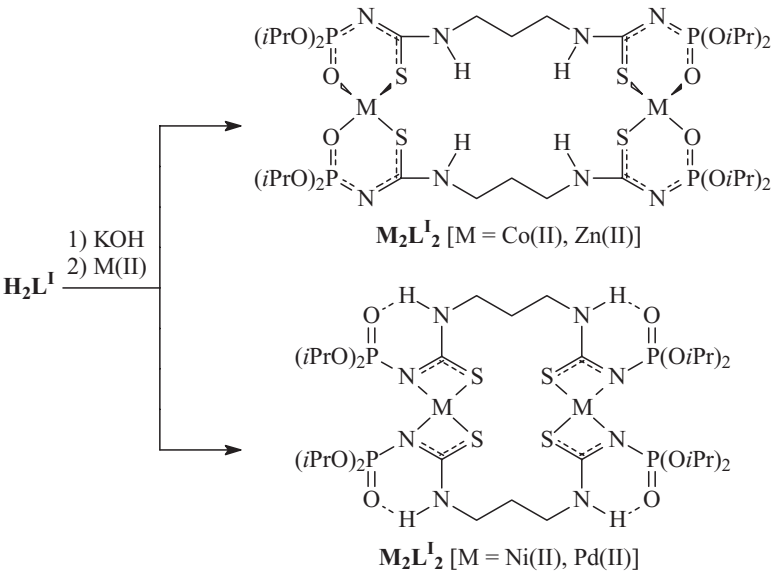
Scheme 1

Previously it has been shown by us[8] that the thiophosphorylated analog $[(i\mathrm{PrO})_2\mathrm{C(S)NHP(S)NHCH_2]_2}$ (**H_2L^{III}**) under KOH treatment converts into salt **K_2L^{III}**, which does not experience any further transformations. It is only under iodine treatment on a salt **K_2L^{III}** solution that an imidazolidine cycle forms. Contrary to this, bis-thiourea **H_2L^{II}** reacts with KOH immediately with a heterocycle formation, which might be due to the presence of more electron-withdrawing P=O groups.

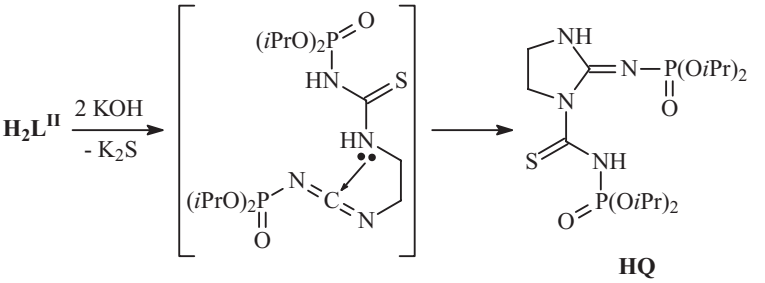
IR, NMR, and UV-Vis Spectroscopy

The IR spectrum of **H_2L^I** contains two absorption bands for the NH group at 3128 and 3281 cm^{-1}. There is an absorption band at 1524 cm^{-1} corresponding to the S=C—N group. The absorption band assigned to the P=O groups is displayed in the characteristic area at 1239 cm^{-1}. The wide absorption band of the ester POC unit of **H_2L^I** at 1008 cm^{-1} confirms the presence of the substituted phosphoryl moiety.

$^{31}P\{^1H\}$ and ^1H NMR spectroscopy data allows us to establish the structure of the obtained compound **H_2L^I** and to confirm the fact of reaction of isothiocyanate with both NH_2 groups of the diamine. There is a singlet signal at –6.9 ppm in the $^{31}P\{^1H\}$ NMR



Scheme 2



Scheme 3

spectrum of $\mathbf{H_2L^I}$. The signal is in the region that is characteristic for *N*-phosphorylated thioamides and thioureas.[6a]

The coordination mode of the ligands in complexes $\mathbf{M_2L^I_2}$ can be reliably followed by the IR spectroscopy. The absorption bands of the P═O group of the anionic ligand $\mathbf{L^I}$ in complexes $\mathbf{Ni_2L^I_2}$ and $\mathbf{Pd_2L^I_2}$ are shifted by 7–12 cm^{-1} to lower wave numbers in comparison with the parent ligand. This shift compares well with the data obtained for 1,3-*N*,*S*-chelates of the Ni(II) and Pd(II) ions with $RNHC(S)NHP(O)(OiPr)_2$ ligands.[9] In contrast to this, involvement of the P═O oxygen atoms in the coordination to the Co(II) and Zn(II) ions in complexes $\mathbf{Co_2L^I_2}$ and $\mathbf{Zn_2L^I_2}$ results in a decrease of the wave number for the P═O stretching mode in the range 97–111 cm^{-1}. This shift compares well with the data obtained for 1,5-*O*,*S*-chelates of the Zn(II)[8,10] and Co(II)[11] ions with $RNHC(S)NHP(O)(OiPr)_2$ and $RR'NC(S)NHP(O)(OiPr)_2$ ligands.

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 3146–3153 cm^{-1}, which is the characteristic range for amide protons

participating in hydrogen bonds. The IR spectra of complexes $\mathbf{Co_2L^I_2}$ and $\mathbf{Zn_2L^I_2}$ exhibit a uniqie absorption band at 3297–3302 cm^{-1}, indicating no hydrogen bonds.

In the IR spectra of complexes there is an intense absorption band at 1543–1566 cm^{-1} corresponding to the conjugated SCN fragment. This fact also confirms the formation of complexes. The wide intensive band of the POC group at 997–1011 cm^{-1} in the IR spectra of $\mathbf{M_2L^I_2}$ confirms the preservation of a structure of the ligand.

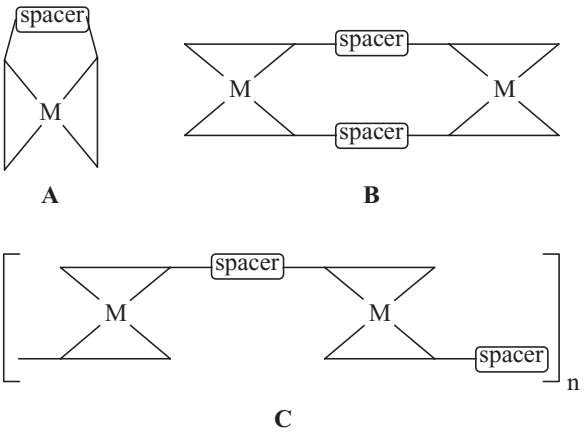
In the $^{31}P\{^1H\}$ spectra of complexes $\mathbf{Ni_2L^I_2}$, $\mathbf{Zn_2L^I_2}$, and $\mathbf{Pd_2L^I_2}$, a singlet signal with a chemical shift characteristic for the amidophosphate environment of the phosphorus nuclei was observed. These signals are low-field shifted in comparison to the corresponding resonance of the parent phosphorylated bis-thiourea. As can been seen in the Experimental section, the $^{31}P\{^1H\}$ resonance in the 1,3-*N*,*S*-chelates is always observed at higher field than for the 1,5-*O*,*S*-analogues.

Only one NH-proton signal was observed in the ^1H NMR spectra of complexes $\mathbf{Ni_2L^I_2}$, $\mathbf{Zn_2L^I_2}$, and $\mathbf{Pd_2L^I_2}$. For the Ni(II) and Pd(II) complexes, the amide proton resonance was observed at 9.25–9.37 ppm and practically in the same region as it was observed for the parent thiourea ($\delta = 9.04$ ppm), while in the case of the Zn(II) complex, the signal for the NH proton is dramatically high-field shifted and shown at 6.29 ppm. This confirms the preservation of the intramolecular hydrogen bonds of the N—H···O=P type in the structure of complexes $\mathbf{Ni_2L^I_2}$ and $\mathbf{Pd_2L^I_2}$ and absence of it in $\mathbf{Zn_2L^I_2}$.

The ^1H NMR spectra of $\mathbf{H_2L^I}$, $\mathbf{Ni_2L^I_2}$, $\mathbf{Zn_2L^I_2}$, and $\mathbf{Pd_2L^I_2}$ contain a set of signals assigned to the $(i\text{PrO})_2\text{P(O)}$ protons. The signals of CH_3 and OCH protons of the acylamidophosphate fragments are 1.28–1.39 and 4.61–4.78 ppm, respectively. The set of signals corresponding to the CH_2 protons at 1.95–2.12 and 3.69–3.84 ppm ranges derives from the propylene moiety.

According to the elemental analysis, complexes have a ratio of M:L = 1:1. Divalent metals can form complexes of 1:1 ML (**A**) and 2:2 M_2L_2 (**B**) compositions with such bipodal ligands. A formation of oligomeric or polymeric composition M_nL_n (**C**) is also possible (Scheme 4).

Available data do not allow us to establish unequivocally what form is realized in a solution and in a solid phase. We suppose that the structure of complexes depends first of all on the length and rigidity of bridging chain between two chelate moieties and



Scheme 4

second on the nature of metal cations. Earlier it has been shown that for complexes of the thiophosphoryl bis-thiourea, containing 1,10-diaza-18-crown-6 fragmnet, with the Co(II) cation[6c] and a number of complexes of similar bifunctional *N*-thiophosphorylthioureas,[6e] dimeric molecules are formed in a growing crystal (**B**).

The $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{Zn_2L^I_2}$ exhibits the only signal. The Zn(II) cation is diamagnetic, and the signals in the $^{31}P\{^1H\}$ NMR spectrum are less sensitive to the environment of the metal cation. That is why both of the forms can have the same chemical shift.

In contrast to zinc(II), nickel(II) and palladium(II) cations do not give tetrahedral forms or adducts, and *cis*- and *trans*-isomers have different signals in spectra, as shown for the complex of RNHC(S)NHP(S)(O*i*Pr)$_2$ (R = *t*Bu, Ph, Ad) with Ni(II) and Pd(II).[12] Nonetheless, the $^{31}P\{^1H\}$ NMR spectra of $\mathbf{Ni_2L^I_2}$ and $\mathbf{Pd_2L^I_2}$ shows a single resonance, which could correspond to the binuclear complex as the only form present in solution.

No NMR spectra of complex $\mathbf{Co_2L^I_2}$ were obtained due to the paramagnetic character of the d^7 Co(II).

The structure of the chelate unit in Co(II) complex $\mathbf{Co_2L^I_2}$ in the CH_2Cl_2 solution was established by UV-Vis spectroscopy. In $\mathbf{Co_2L^I_2}$ there is an absorption band with peaks at 558, 611, and 658 nm and with molar extinction coefficient (ε) 512, 565, and 337 l mol^{-1} cm^{-1}, respectively. The specified absorption band corresponds to a transition from the basic state $^4A_2$ to a $^4T_1$(P) state. The fine structure is caused by spin–orbital interaction, as a result of which, first, there is a splitting of the state $^4T_1$(P) and, second, there are resolved transitions in the next doublet states with the same intensity. Other possible transitions $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$(F)– are outside of the visible area. Data of UV-spectroscopy confirm the tetrahedral environment of the Co(II) cation in complex $\mathbf{Co_2L^I_2}$. Absorption is observed in the red region of the spectrum, which explains the dark blue color of the Co(II) complex. It is necessary to note that the values of ε are approximately twice more than for the Co(II) complex with *N*-phosphorylated monothioureas.[11] This fact testifies the formation of the complex of the $\mathbf{Co_2L^I_2}$ composition. Thus, it is reasonable to assume that complex $\mathbf{Co_2L^I_2}$ exists as the structure **B**, shown in Scheme 4.

Thus, the structure of complexes $\mathbf{M_2L^I_2}$, containing propylene bridging fragments, is reliably proved by comparison of the IR and $^{31}P\{^1H\}$, ^1H NMR spectra of these complexes with the spectra of $\mathbf{H_2L^I}$. Obtained IR, NMR, and UV spectral data are evidence of the chelate core formation with participation of C=S and P=O or P–N groups and the metal cation.

The IR spectrum of **HQ** contains two absorption bands for the NH group at 3225 and 3304 cm^{-1}. There is an absorption band at 1532 cm^{-1} corresponding to the S=C–N group. The absorption band assigned to the P=O groups is displayed at 1223 cm^{-1}. The characteristic band for the C=N group is shown at 1657 cm^{-1}. The wide absorption band of the ester POC unit of **HQ** at 986–1017 cm^{-1} confirms the presence of the substituted phosphoryl moieties.

The ^{31}P NMR spectrum of **HQ** contains two signals of equal intensity, with chemical shifts of –5.9 and 6.8 ppm, corresponding to the phosphorus atoms in amidothiophosphate and imidothiophosphate environments,[6a] respectively. The signals represent a doublet of triplets and a triplet with characteristic $^3J_{POCH}$ and $^2J_{PNH}$ constants. A shift of the signal of the PNH group proton up to 12.04 ppm in the ^1H NMR spectrum specifies the O=P–NH···N–P=O hydrogen bond in solution.[8] The ^1H NMR spectrum of **HQ** contains a double set of isopropoxyl group signals. The signals for the NCH_2 protons were observed at 3.17–4.06 ppm.

CONCLUSIONS

The data presented allow us to confirm that the complexation properties of the bis-thiourea $\mathbf{H_2L^I}$ depend on the nature of the metal cation. The deprotonated ligand $\mathbf{L^I}$ shows 1,5-*O*,*S*-coordination mode towards Co(II) and Zn(II), while 1,3-*N*,*S*-coordination takes place in the case of Ni(II) and Pd(II). The formation of the intramolecular hydrogen bonds N—H···O=P is a necessary condition for the 1,3-*N*,*S*-isomer stabilization in a square–planar complexes of Ni(II) and Pd(II). 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 the ligand's field strength. Complexes $\mathbf{Ni_2L^I_2}$ and $\mathbf{Pd_2L^I_2}$ are the first example of bis-thiourea $[RR'P(O)NHC(S)NH]_2Z$ complexes, where the chelate moieties are coordinated in a 1,3-*N*,*S*-fashion.

Bis-thiourea $\mathbf{H_2L^{II}}$, upon treatment with KOH, converts into the iminoimidazolidine **HQ**, containing the *N*-phosphorylthiourea fragment.

Compounds $\mathbf{H_2L^{I,II}}$ and **HQ** may be used as the selective analytical reagent, especially for the determination of transition metals in complex interfering matrices. All the obtained ligands and complexes may be also used as precursors to supramolecular compounds.

EXPERIMENTAL

O,*O*′-diisopropylphosphoric acid isothiocyanate $(i\mathrm{PrO})_2\mathrm{P(O)NCS}$ was synthesized as previously described.[13] Bis-thiourea $\mathbf{H_2L^{II}}$ was synthesized as previously described.[14]

Synthesis of H_2L^I

A solution of 1,3-propylendiamine (0.148 g, 2 mmol) in anhydrous CH_2Cl_2 (10 mL) was treated with vigorous stirring with a solution of diisopropoxyphosphoryl isothiocyanate $(i\mathrm{PrO})_2\mathrm{P(O)NCS}$ (0.981 g, 4.4 mmol, 10% excess) in anhydrous CH_2Cl_2 (10 mL). The mixture was stirred for an additional 30 min to complete the reaction. The solvent was removed in a vacuum, and the product was purified by crystallization from dichloromethane by *n*-hexane. Yield: 0.905 g (87%). Mp 72°C. ^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (d, $^3J_{H,H} = 6.1$ Hz, 12H, CH_3), 1.37 (d, $^3J_{H,H} = 6.0$ Hz, 12H, CH_3), 2.00 (quin, $^3J_{H,H} = 7.1$ Hz, 2H, $CH_2CH_2CH_2$), 3.69 (q, $^3J_{H,H} = 6.4$ Hz, 4H, $CH_2CH_2CH_2$), 4.69 (d sept, $^3J_{POCH} = 7.0$ Hz, $^3J_{H,H} = 6.1$ Hz, 4H, OCH), 6.67 (d, $^2J_{PNH} = 7.0$ Hz, 2H, P(O)NH), 9.04 (t, $^3J_{H,H} = 6.0$ Hz, 2H, NH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = -6.9$ ppm. IR (KBr): $\nu = 1008$ (POC), 1239 (P=O), 1524 (S=C—N), 3128, 3281 (NH) cm^{-1}. Calcd. for $C_{17}H_{38}N_4O_6P_2S_2$ (520.58): C, 39.22; H, 7.36; N, 10,76. Found: C, 39.13; H, 7.41; N, 10.69.

Synthesis of $M_2L^I_2$

A suspension of $\mathbf{H_2L^I}$ (0.364 g, 0.7 mmol) in aqueous EtOH (10 mL) was mixed with an aqueous EtOH solution of potassium hydroxide (0.086 g, 1.54 mmol, 10% excess). An aqueous EtOH (10 mL) solution of $CoCl_2$ (0.118 g), $NiCl_2$ (0.118 g), $ZnCl_2$ (0.124 g), or an acetonitrile solution $Pd(PhCN)_2Cl_2$ (0.349 g, 0.91 mmol, 30% excess) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 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 dark blue ($\mathbf{Co_2L^I_2}$), violet ($\mathbf{Ni_2L^I_2}$), colourless ($\mathbf{Zn_2L^I_2}$),

and red ($\mathbf{Pd_2L^I_2}$) precipitate was isolated from dichloromethane by *n*-hexane. All yields are given with respect to $\mathbf{H_2L^I}$.

$\mathbf{Co_2L^I_2}$. Yield: 0.558 g (69%). Mp 81°C. UV-Vis spectrum, [λ_{max}, nm (ε, 1 mol^{-1} dm^3 cm^{-1})]: 558 (512), 611 (565), 658 (337). IR: ν = 1002 (POC), 1142 (P=O), 1564 (SCN), 3302 (NH) cm^{-1}. Calcd. for $C_{34}H_{72}Co_2N_8O_{12}P_4S_4$ (1154.99): C, 35.36; H, 6.28; N, 9.70. Found: C, 35.23; H, 6.33; N, 9.79.

$\mathbf{Ni_2L^I_2}$. Yield: 0.671 g (83%). Mp 119°C. ^{1}H NMR: δ = 1.32 (d, $^3J_{H,H}$ = 6.2 Hz, 24H, CH_3), 1.39 (d, $^3J_{H,H}$ = 6.1 Hz, 24H, CH_3), 2.07 (quin, $^3J_{H,H}$ = 6.8 Hz, 4H, $CH_2CH_2CH_2$), 3.75 (q, $^3J_{H,H}$ = 6.2 Hz, 8H, $CH_2CH_2CH_2$), 4.78 (d sept, $^3J_{POCH}$ = $^3J_{H,H}$ = 6.3 Hz, 8H, OCH), 9.37 (br. s, 4H, NH) ppm. ^{31}P{^{1}H} NMR: δ = 1.4 ppm. IR: ν = 997 (POC), 1232 (P=O), 1557 (SCN), 3153 (NH) cm^{-1}. Calcd. for $C_{34}H_{72}N_8Ni_2O_{12}P_4S_4$ (1154.51): C, 35.37; H, 6.29; N, 9.71. Found: C, 35.50; H, 6.21; N, 9.73.

$\mathbf{Zn_2L^I_2}$. Yield: 0.613 g (75%). Mp 94°C. ^{1}H NMR: δ = 1.28 (d, $^3J_{H,H}$ = 6.0 Hz, 48H, CH_3), 2.12 (br. s, 4H, $CH_2CH_2CH_2$), 3.79 (q, $^3J_{H,H}$ = 6.1 Hz, 8H, $CH_2CH_2CH_2$), 4.74 (d sept, $^3J_{POCH}$ = $^3J_{H,H}$ = 6.2 Hz, 8H, OCH), 6.29 (br. s, 4H, NH) ppm. ^{31}P{^{1}H} NMR: δ = 6.2 ppm. IR: ν = 1011 (POC), 1128 (P=O), 1566 (SCN), 3297 (NH) cm^{-1}. Calcd. for $C_{34}H_{72}N_8O_{12}P_4S_4Zn_2$ (1167.89): C, 34.97; H, 6.21; N, 9.59. Found: C, 34.80; H, 6.29; N, 9.63.

$\mathbf{Pd_2L^I_2}$. Yield: 0.823 g (94%). Mp 147°C. ^{1}H NMR: δ = 1.35 (d, $^3J_{H,H}$ = 6.1 Hz, 48H, CH_3), 1.95 (br. s, 4H, $CH_2CH_2CH_2$), 3.84 (br. s, 8H, $CH_2CH_2CH_2$), 4.61 (d sept, $^3J_{POCH}$ = $^3J_{H,H}$ = 6.2 Hz, 8H, OCH), 9.25 (br. s, 4H, NH) ppm. ^{31}P{^{1}H} NMR: δ = 2.3 ppm. IR: ν = 1009 (POC), 1227 (P=O), 1543 (SCN), 3146 (NH) cm^{-1}. Calcd. for $C_{34}H_{72}N_8O_{12}P_4Pd_2S_4$ (1249.97): C, 32.67; H, 5.81; N, 8.96. Found: C, 32.82; H, 5.73; N, 8.87.

Synthesis of HQ

A suspension of $\mathbf{H_2L^{II}}$ (0.354 g, 0.7 mmol) in aqueous EtOH (10 mL) was mixed with an aqueous EtOH solution of potassium hydroxide (0.086 g, 1.54 mmol, 10% excess). The mixture was stirred at room temperature for a further 3 h. Then the solvent was removed in vacuo. The residue was recrystallized from a methylene chloride/*n*-hexane mixture, and compound **HQ** was isolated as colorless crystals. Yield: 0.278 g (84%). MP 109°C. ^{1}H NMR: δ = 1.32–1.46 (m, 24H, CH_3), 3.17–4.06 (m, 4H, CH_2), 4.63 (d sept, $^3J_{POCH}$ = 9.5 Hz, $^3J_{H,H}$ = 6.1 Hz, 2H, OCH), 4.87 (d sept, $^3J_{POCH}$ = 9.1 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH), 8.27 (s, 1H, NH), 12.04 (d, $^2J_{PNH}$ = 11.8 Hz, 1H, NHP) ppm. ^{31}P NMR: δ = –5.9 (d trip, $^3J_{POCH}$ = 9.7 Hz, $^2J_{PNH}$ = 11.9 Hz, 1P, PNH), 6.8 (t, $^3J_{POCH}$ = 9.4 Hz, 1P, PN) ppm. IR: ν = 986, 1017 (POC), 1223 (P=O), 1532 (S=C–N), 1657 (C=N), 3225, 3304 (NH) cm^{-1}. Calcd. for $C_{16}H_{34}N_4O_6P_2S$ (472.48): C, 40.67; H, 7.25; N, 11.86. Found: C, 40.84; H, 7.19; N, 11.83.

Physical Measurements

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. NMR spectra ($CDCl_3$) were obtained on a Varian Unity-300 NMR spectrometer at 25°C. ^{1}H and ^{31}P{^{1}H} spectra were recorded at 299.948 and 75.429 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Electronic spectra of absorption in 0.001 M solution of CH_2Cl_2 were measured on a

Perkin-Elmer Lambda-35 spectrometer in the range 200–1000 nm. Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyzer.

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