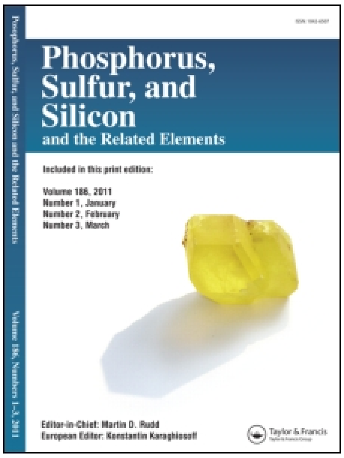

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Complexes of *N*-Phosphorylated Thioureas RNHC(S)NHP(O)(O*i*Pr)$_2$ (R = 2-MeC$_6$H$_4$, 2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$) With Nickel(II)

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COMPLEXES OF *N*-PHOSPHORYLATED THIOUREAS $RNHC(S)NHP(O)(O\textit{i}Pr)_2$ (R = $2\text{-}MeC_6H_4$, $2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$) WITH NICKEL(II)

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The reaction of* O,O′*-diisopropylphosphoric acid isothiocyanate* $(\textit{i}PrO)_2P(O)NCS$ *with 2-methylaniline* $2\text{-}MeC_6H_4NH_2$*, 2,6-dimethylaniline* $2,6\text{-}Me_2C_6H_3NH_2$*, or 2,4,6-trimethylaniline* $2,4,6\text{-}Me_3C_6H_2NH_2$ *leads to the* N*-phosphorylated thioureas* $RNHC(S)NHP(O)(O\textit{i}Pr)_2$ *(R =* $2\text{-}MeC_6H_4-$*,* HL^{I}*;* $2,6\text{-}Me_2C_6H_3-$*,* HL^{II}*;* $2,4,6\text{-}Me_3C_6H_2-$*,* HL^{III}*). Reaction of the potassium salts of* HL^{I-III} *with Ni(II) in aqueous EtOH leads to* $[Ni(L^{I-III}\text{-}N,S)_2]$ *(*$[NiL^{I-III}{}_2]$*) chelate complexes. The compounds obtained were investigated by* ^{1}H*,* $^{31}P\{^{1}H\}$ *NMR spectroscopy and microanalysis. The molecular structure of the thiourea* HL^{III} *was elucidated by single crystal X-ray diffraction analysis. Single crystal X-ray diffraction studies showed that* HL^{III} *forms both intra- and intermolecular hydrogen bonds, which in turn leads to the formation of polymeric chains. One of the intermolecular hydrogen bonds is of the type* $N-H\cdots S$*. Moreover, the formation of intermolecular* $C-H\cdots\eta^{6}$*-phenyl interactions was established.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Crystal structure; hydrogen bond; nickel(II); phosphorylthiourea

INTRODUCTION

There have been a great number of studies of the coordination chemistry of imidodiphosphinates $R_2P(X)NHP(Y)R'_2$ (**HZ**) (X, Y = O, S; R, R′ = alkyl, aryl) with various metal cations.[1–17] In particular, the complexation properties of **HZ** towards Ni(II) are of great interest due to the coordination versatility: octahedral, tetrahedral, and square-planar. The overwhelming majority of Ni(II) complexes contain symmetric anionic ligands **Z**,

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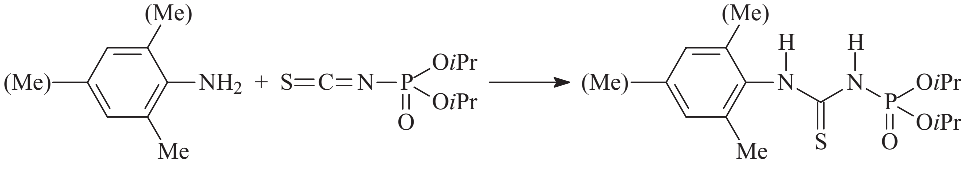
which contain both identical donor atoms (X = Y) and substituents (R = R′) simultaneously,[9–16] although some studies on unsymmetrical **HZ** ligands have been reported.[17] However, these investigations have been devoted to either mixed chalcogens or mixed substituent complexes. Ni(II) complexes usually contain a square-planar or octahedral complex core. The tetrahedral environment in Ni(II) complexes with **HZ** is rare and not well understood, although some examples have been reported.[12–17]

Recently, we reported some synthetic results as a preliminary communication.[18] In this article, we report the synthesis and characterization of *N*-phosphorylated thioureas $RNHC(S)NHP(O)(OiPr)_2$ (R = $2\text{-}MeC_6H_4$–, **HL^I**; $2,6\text{-}Me_2C_6H_3$–, **HL^II**; $2,4,6\text{-}Me_3C_6H_2$–, **HL^III**). The reaction of the potassium salts of $\mathbf{HL^{I–III}}$ with Ni(II) in aqueous EtOH leads to $[Ni(L^{I–III}\text{-}N,S)_2]$ ($[\mathbf{NiL^{I–III}_2}]$) chelate complexes.

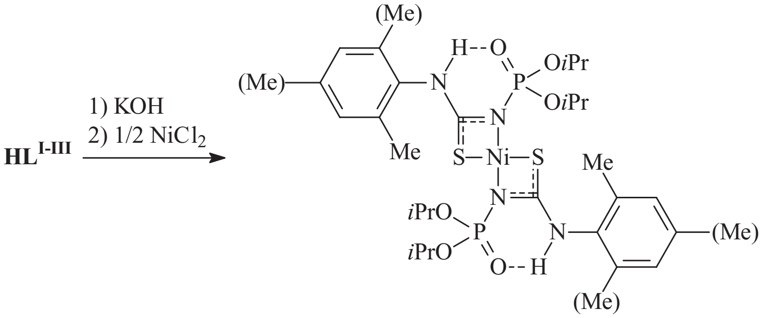
RESULTS AND DISCUSSION

The compounds $\mathbf{HL^{I–III}}$ were synthesized by the treatment of 2-methylaniline, 2,6-dimethylaniline, or 2,4,6-trimethylaniline with the isothiocyanate $(iPrO)_2P(O)NCS$ (Scheme 1). Complexes $[\mathbf{NiL^{I–III}_2}]$ were prepared by the following procedure: the ligand was deprotonated in situ using KOH, followed by reaction with $NiCl_2$ (Scheme 2). The compounds obtained are crystalline solids, which are soluble in most polar solvents. The formation of $\mathbf{HL^{I–III}}$ by the addition reaction of the NH_2 group of the corresponding amine and $(iPrO)_2P(O)NCS$ and the coordination mode of the anionic ligands in $[\mathbf{NiL^{I–III}_2}]$ were investigated by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy; their compositions were established by elemental analysis.



HL^I-III

Scheme 1



$[\mathbf{NiL^{I-III}_2}]$

Scheme 2

The $^{31}P\{^1H\}$ NMR spectra of **HL$^{I–III}$** each contain a singlet signal at −6.4, −6.3, and −5.9 ppm, respectively, which is typical for *N*-phosphoryl thioureas.[19] The ^1H NMR spectra of the thioureas contain a set of signals for the *i*Pr protons: a doublet or two doublets for the CH_3 protons at 1.39–1.46 ppm and a doublet of septets for the CH protons in the area 4.77–4.87 ppm. The Me proton signals were observed at 2.24–2.32 ppm. The aromatic ring and PNH proton signals are at 6.91–7.61 ppm. Signals for the arylNH protons in the spectra are at 9.42–10.07 ppm. These signals are in a low-field area because of the hydrogen bonds' formation of the arylN—H···O = P type.

The Ni(II) atom in the complexes **[NiL$^{I–III}$$_2$]** was found in a square-planar N_2S_2 environment formed by the nitrogen and sulfur atoms of the N—P and C═S groups. Earlier studies on the 1,5-*S*,*S'*-complexes of the Ni(II) ion with *N*-thiophosphorylated thiourea PhNHC(S)NHP(S)(O*i*Pr)$_2$ in CD_2Cl_2 solution have shown a multicomponent 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.

In the $^{31}P\{^1H\}$ spectra of the complexes **[NiL$^{I–III}$$_2$]**, a singlet signal with a chemical shift at 2.0–2.6 ppm was observed. The signal is characteristic for the amidophosphate environment of the phosphorus nuclei.[19] These signals are 8.3–8.5 ppm low-field shifted in comparison to the corresponding resonance of the parent phosphorylated thiourea. It is noteworthy that the $^{31}P\{^1H\}$ resonance in the spectra of the complexes **[NiL$^{I–III}$$_2$]** is observed in the region characteristic for the 1,3-*N*,*S*-chelate complexes of Ni(II) with RNHC(S)NHP(O)(O*i*Pr)$_2$ ligands.[20]

The ^1H NMR spectra of the complexes **[NiL$^{I–III}$$_2$]** contain only signals that correspond to the proposed structures. The spectra contain a set of signals for the *i*Pr protons: two doublets for the CH_3 protons at 1.30–1.62 ppm and a doublet of septets for the CH protons at 4.59–4.66 ppm. The signals for the Me protons are observed at 2.21–2.36 ppm. The aromatic ring proton signals in the spectra of **[NiL$^{I–III}$$_2$]** are at 6.91–7.36 ppm. The signal for the NHP group proton is absent in the ^1H NMR spectra of **[NiL$^{I–III}$$_2$]**. This confirms the presence of the ligand anionic form in the structure of complexes. Signals for the arylNH protons in the spectra of the complexes are at 10.38–10.51. These signals are in a low-field area because of the hydrogen bonds' formation of the arylN—H···O═P type.

Crystals of **HL^{III}** were obtained by recrystallization from dichloromethane–*n*-hexane solution (Table I). The molecular conformation and geometric parameters are shown in Figure 1.

The compound **HL^{III}** crystallizes in the space group *P*–1. The asymmetric unit contains two independent molecules. The parameters of the C═S, C—N, P—N, and P═O bonds observed for **HL^{III}** (Figure 1) are in the typical range for *N*-phosphorylated thiourea derivatives.[19] The S—C—N—P backbone in the crystal phase has an *E*-conformation. The aryl fragment is almost orthogonal to the N—C(S)—N—P plane. The crystal structure is stabilized by intramolecular hydrogen bonds of the types N(2)—H(2)···O(3)[O(3′)]—P(1) and N(2A)—H(2A)···O(3A)—P(1A) (Figure 1, see also Table S1, Supplemental Materials, available online). Two independent molecules form a dimer due to intermolecular hydrogen bonds of the types N(2)—H(2)···O(3A)—P(1A) and N(2A)—H(2A)···O(3)[O(3′)]—P(1) (Figure 1, Table S1). Yet another mode of aggregation is found for this dimer. Two independent molecules form interactions between the OCH hydrogen atoms and the aryl rings of an adjacent molecule (Table S2, Supplemental Materials). Furthermore, dimers form polymeric chains due to the intermolecular hydrogen bonds of the types

Table I Crystal structure and data refinement parameters for HL^{III}

Empirical formula	$C_{16}H_{27}N_2O_3PS$
Formula weight (g mol^{-1})	358.43
Temperature (K)	173(2)
Crystal system	Triclinic
Space group	P–1
a (Å)	10.6334(7)
b (Å)	13.4890(8)
c (Å)	15.7710(10)
α (°)	82.491(5)
β (°)	70.663(5)
γ (°)	67.113(5)
V (Å^3)	1966.4(2)
Z	4
D_{calc} (Mg m^{-3})	1.211
Absorption coefficient, μ (mm^{-1})	0.260
F(000)	768
Crystal size (mm)	0.32 × 0.26 × 0.21
Recording range, θ (°)	3.55–25.59
Number of recorded reflections	21017
Number of recorded independent reflections	7336 [R(int) = 0.0465]
Final R indices [I > 2sigma(I)]	R1 = 0.0389, wR2 = 0.0937
R indices (all data)	R1 = 0.0568, wR2 = 0.0989
S	0.951

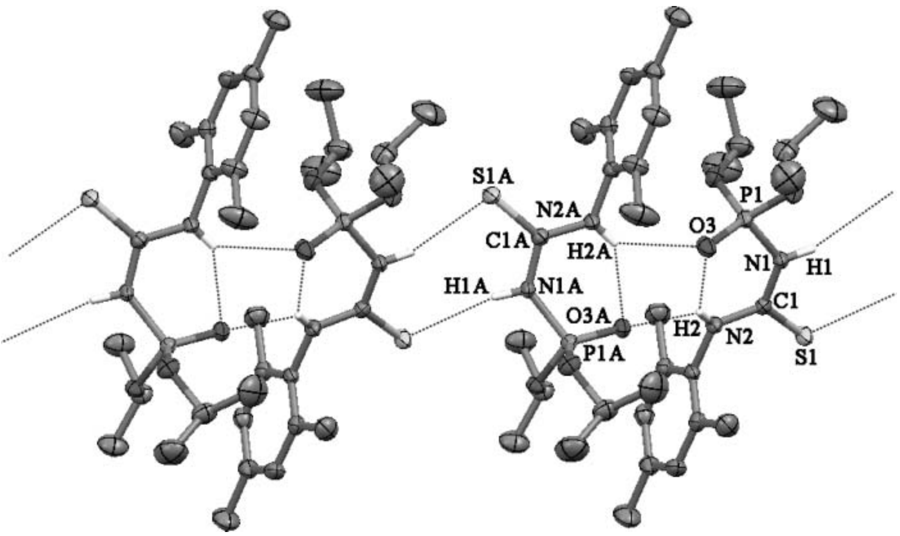


Figure 1 Thermal ellipsoid representation of $\mathbf{HL^{III}}$. Ellipsoids are drawn at the 50% probability level. H-atoms, not involved in hydrogen bonding, are omitted for clarity. Selected bond distances (Å) and angles (°): P(1)–O(3) 1.482(2), P(1)–O(3′) 1.391(7), P(1)–N(1) 1.656(2), S(1)–C(1) 1.675(2), N(1)–C(1) 1.383(2), N(2)–C(1) 1.333(2), P(1A)–O(3A) 1.4656(14), P(1A)–N(1A) 1.658(2), S(1A)–C(1A) 1.673(2), N(1A)–C(1A) 1.378(2), N(2A)–C(1A) 1.334(2); O(3)–P(1)–N(1) 113.29(9), O(3′)–P(1)–N(1) 116.3(4), C(1)–N(1)–P(1) 128.61(14), N(2)–C(1)–N(1) 117.1(2), N(1)–C(1)–S(1) 119.45(14), N(2)–C(1)–S(1) 123.44(13), O(3A)–P(1A)–N(1A) 113.02(8), C(1A)–N(1A)–P(1A) 128.27(14), N(2A)–C(1A)–N(1A) 116.8(2), N(1A)–C(1A)–S(1A) 120.05(14), N(2A)–C(1A)–S(1A) 123.11(14).

N(1)—H(1)···S(1A)#1—C(1A)#1 and N(1A)—H(1A)···S(1)#2—C(1)#2 (Figure 1, Table S1).

CONCLUSIONS

In summary, we have demonstrated the syntheses of three new *N*-phosphorylated thioureas **HL$^{I–III}$** by addition of phosphorylisothiocyanate to the corresponding amine. Single crystal X-ray diffraction studies showed the thiourea **HL^{III}** to form both intra- and intermolecular hydrogen bonds, which in turn lead to polymeric chain formation. Moreover, according to the X-ray data of **HL^{III}**, the formation of the intermolecular C—H···η^6-phenyl interactions were established.

The data presented allow us to confirm that, at least for the investigated *N*-phosphorylthiourea ligands **HL$^{I–III}$**, the formation of the intramolecular hydrogen bonds N—H···O = P is a necessary condition for the 1,3-*N*,*S*-isomer stabilization in the square-planar complexes of Ni(II) **[NiL$^{I–III}_2$]**. 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.

EXPERIMENTAL

Physical Measurements

NMR spectra in $CDCl_3$ were obtained on a Bruker Avance 300 MHz spectrometer at 25°C. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P{^{1}H}). Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer.

Synthesis of HL$^{I–III}$

A solution of 2-methylaniline, 2,6-dimethylaniline, or 2,4,6-trimethylaniline (5 mmol; 0.54, 0.61, or 0.68 g) in anhydrous CH_2Cl_2 (15 mL) was treated under vigorous stirring with a solution of $(i\text{PrO})_2\text{P(O)NCS}$ (6 mmol, 1.34 g) in the same solvent. The mixture was stirred for 1 h. The solvent was removed under vacuum, and the product was purified by recrystallization from a 1:5 (v/v) mixture of dichloromethane and *n*-hexane.

HL^{I}. Yield: 1.42 g (86%); mp: 72°C; Anal. Calcd for $C_{14}H_{23}N_2O_3PS$ (330.38): C, 50.90; H, 7.02; N, 8.48; Found: C, 50.96; H, 6.95; N, 8.52; ^{1}H NMR δ (ppm): 1.39 (d, $^3J_{H,H} = 6.1$ Hz, 12H, CH_3, *i*Pr), 2.31 (s, 3H, CH_3, Me), 4.83 (d. sept, $^3J_{POCH} = 7.1$ Hz, $^3J_{H,H} = 6.0$ Hz, 2H, OCH), 6.94–7.61 (m, overlapped with the solvent signal, C_6H_4 + PNH), 9.42 (s, 1H, NH); ^{31}P{^{1}H} NMR δ (ppm): −6.4.

HL^{II}. Yield: 1.62 g (94%); mp: 89°C; Anal. Calcd for $C_{15}H_{25}N_2O_3PS$ (344.41): C, 52.31; H, 7.32; N, 8.13; Found: C, 52.20; H, 7.37; N, 8.05; ^{1}H NMR δ (ppm): 1.43 (d, $^3J_{H,H}$ = 6.1 Hz, 6H, CH_3, *i*Pr), 1.46 (d, $^3J_{H,H} = 6.2$ Hz, 6H, CH_3, *i*Pr), 2.32 (s, 6H, CH_3, Me), 4.87 (d. sept, $^3J_{POCH} = 7.2$ Hz, $^3J_{H,H} = 6.1$ Hz, 2H, OCH), 7.09–7.36 (m, overlapped with the solvent signal, C_6H_3 + PNH), 9.59 (s, 1H, NH); ^{31}P{^{1}H} NMR δ (ppm): −6.3.

HL^{III}. Yield: 1.29 g (72%); mp: 97°C; Anal. Calcd for $C_{16}H_{27}N_2O_3PS$ (358.44): C, 53.62; H, 7.59; N, 7.82; Found: C, 53.71; H, 7.68; N, 7.89; ^{1}H NMR δ (ppm): 1.42 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3, *i*Pr), 2.24 (s, 6H, CH_3, Me), 2.29 (s, 3H, CH_3, Me), 4.77 (d. sept,

$^{3}J_{\mathrm{POCH}} = 6.8$ Hz, $^{3}J_{\mathrm{H,H}} = 6.2$ Hz, 2H, OCH), 6.91 (s, 2H, C_6H_2), 7.02 (br. s, 1H, PNH), 10.07 (s, 1H, NH); $^{31}P\{^{1}H\}$ NMR δ (ppm): −5.9.

Synthesis of [NiL$^{\mathrm{I-III}}_2$]

A suspension of **HL$^{\mathrm{I-III}}$** (3 mmol; 0.99, 1.03, or 1.08 g) in aqueous EtOH (10 mL) was mixed with an aqueous EtOH solution of potassium hydroxide (3.3 mmol, 0.18 g). An aqueous EtOH (10 mL) solution of $NiCl_2$ (1.9 mmol, 0.25 g) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and then left overnight. The resulting complex was extracted with dichloromethane, washed with water, and dried with anhydrous $MgSO_4$. The solvent was then removed under vacuum. Violet **[NiL$^{\mathrm{I-III}}_2$]** crystals were isolated from dichloromethane by *n*-hexane.

[NiL$^{\mathrm{I}}_2$]. Yield: 0.89 g (83%); mp: 118°C; Anal. Calcd for $C_{28}H_{44}N_4NiO_6P_2S_2$ (717.44): C, 46.88; H, 6.18; N, 7.81; Found: C, 46.97; H, 6.14; N, 7.85; ^{1}H NMR δ (ppm): 1.33 (d, $^{3}J_{\mathrm{H,H}} = 6.0$ Hz, 12H, CH_3, *i*Pr), 1.57 (d, $^{3}J_{\mathrm{H,H}} = 6.2$ Hz, 12H, CH_3, *i*Pr), 2.36 (s, 6H, CH_3, Me), 4.62 (d. sept, $^{3}J_{\mathrm{POCH}} = 6.8$ Hz, $^{3}J_{\mathrm{H,H}} = 6.2$ Hz, 4H, OCH), 6.91–7.36 (m, overlapped with the solvent signal, C_6H_4), 10.38 (s, 2H, NH); $^{31}P\{^{1}H\}$ NMR δ (ppm): 2.1.

[NiL$^{\mathrm{II}}_2$]. Yield: 0.86 g (77%); mp: 91°C; Anal. Calcd for $C_{30}H_{48}N_4NiO_6P_2S_2$ (745.49): C, 48.33; H, 6.49; N, 7.52; Found: C, 48.24; H, 6.52; N, 7.46; ^{1}H NMR δ (ppm): 1.36 (d, $^{3}J_{\mathrm{H,H}} = 6.2$ Hz, 12H, CH_3, *i*Pr), 1.62 (d, $^{3}J_{\mathrm{H,H}} = 6.1$ Hz, 12H, CH_3, *i*Pr), 2.34 (s, 12H, CH_3, Me), 4.59 (d. sept, $^{3}J_{\mathrm{POCH}} = 7.0$ Hz, $^{3}J_{\mathrm{H,H}} = 6.2$ Hz, 4H, OCH), 7.01–7.32 (m, overlapped with the solvent signal, C_6H_3), 10.51 (s, 2H, NH); $^{31}P\{^{1}H\}$ NMR δ (ppm): 2.0.

[NiL$^{\mathrm{III}}_2$]. Yield: 1.11 g (96%); m. p.: 128°C; Anal. Calcd for $C_{32}H_{52}N_4NiO_6P_2S_2$ (773.55): C, 49.69; H, 6.78; N, 7.24; Found: C, 49.60; H, 6.83; N, 7.21; ^{1}H NMR δ (ppm): 1.30 (d, $^{3}J_{\mathrm{H,H}} = 6.2$ Hz, 12H, CH_3, *i*Pr), 1.59 (d, $^{3}J_{\mathrm{H,H}} = 6.1$ Hz, 12H, CH_3, *i*Pr), 2.21 (s, 12H, CH_3, Me), 2.32 (s, 6H, CH_3, Me), 4.66 (d. sept, $^{3}J_{\mathrm{POCH}} = 6.5$ Hz, $^{3}J_{\mathrm{H,H}} = 6.0$ Hz, 4H, OCH), 6.98 (s, 4H, C_6H_2), 10.43 (s, 2H, NH); $^{31}P\{^{1}H\}$ NMR δ (ppm): 2.6.

Crystal Structure Determination and Refinement

The X-ray data for **HL$^{\mathrm{III}}$** were collected on a STOE IPDS-II diffractometer with graphite-monochromatized Mo-K$_\alpha$ radiation generated by a fine-focus X-ray tube operated at 50 kV and 40 mA. The images were indexed, integrated, and scaled using the X-Area data reduction package.[21] Data were corrected for absorption using the PLATON program.[22] The structures were solved by direct methods using the SHELXS-97 program[23] and refined first isotropically and then anisotropically using SHELXL-97.[23] Hydrogen atoms were revealed from $\Delta\rho$ maps, and those bonded to C were refined using appropriate riding models. H atoms bonded to N were freely refined.

CCDC 737532 (**HL$^{\mathrm{III}}$**) contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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