# The influence of an intramolecular hydrogen bond on the 1,3-*N*,*S*-coordination of crown ether-containing *N*-phosphorylthiourea with $Ni^{II}$†

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***Received (in Victoria, Australia) 10th June 2009, Accepted 30th August 2009***
***First published as an Advance Article on the web 1st October 2009***
**DOI: 10.1039/b9nj00252a**

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Published on 01 October 2009 on http://pubs.rsc.org | doi:10.1039/B9NJ00252A

Reaction of the lithium salt of *N*-phosphorylated thiourea [4′-benzo-15-crown-5]-NHC(S)NHP(O)(O*i*Pr)$_2$ (**HL$^I$**) with $Ni^{II}$ leads to the chelate complex **[NiL$^I_2$]**. 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 **L$^I$** ligands. Reaction of **[NiL$^I_2$]** and its non-crown ether-containing analog Ni[PhNHC(S)NP(O)(O*i*Pr)$_2$]$_2$ (**[NiL$^{II}_2$]**) with 2,2′-bipyridine (**bipy**) and 1,10-phenanthroline (**phen**) leads to the **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]** heteroligand complexes. The coordination mode is preserved for the phosphorus-containing ligands. The extraction properties of the crown ether-containing compounds towards alkali metal picrates were investigated. The molecular structures of **HL$^I$**, **[NiL$^I_2$]** and **[Ni(bipy)L$^{II}_2$]** were elucidated by X-ray diffraction.

## Introduction

The metal–organic architectures formed by d-metal cations and bifunctional ligands, *e.g.* bis-β-diketonates or bis-*N*-acylthioureas),[1–6] are of great interest due to their magnetic, gas storage or catalytic properties. In relation to this, the idea of using crown ethers armed with exocyclic chelating groups as ligands for the building of such structures seems rather attractive.

The combination of a crown ether moiety and exocyclic donor groups in a molecule is an effective way to design selective complexing agents.[7–10] Metal-containing derivatives of crown ethers are used as molecule-based ion probes,[3,11,12] and as agents for molecular recognition and the transportation of anions and ion pairs.[13,14]

The derivatives of various crown ethers bearing one or two thioacylamidophosphate fragments, –C(S)NHP(X)(OR)$_2$ (X = O, S), their complexes with $Co^{II}$, $Ni^{II}$, $Pd^{II}$, $Cu^{I}$ and $Cd^{II}$ cations,[15–20] and the selective binding of sodium cations[21] were reported previously by us. Ligands containing two essentially different complexing moieties, such as a chelating fragment and a macrocycle, possess the ability to form complexes with both alkaline and transition metal cations.

The numerous examples reported by our group[15–20] indicate that the RC(S)NHP(X)R′$_2$ fragment has a propensity for 1,5-*S*,*X*-chelate formation. However, these investigations showed that ligands of the general formula RNHC(S)NHP(O)(O*i*Pr)$_2$ form 1,3-*N*,*S*-chelates with $Ni^{II}$ and $Pd^{II}$ cations.[22–24] The higher stability of the 1,3-*N*,*S*- relative to the 1,5-*O*,*S*-isomer is caused by (i) a higher crystal field stabilization energy for the low-spin $d^8$ [M{RN(H)C(S)NP(O)(O*i*Pr)$_2$-*N*,*S*}$_2$] complexes and (ii) the formation of strong (20–25 kJ mol$^{-1}$)[22] intramolecular NH···O=P hydrogen bonds in the 1,3-*N*,*S*-chelate complexes.

It was interesting to use the coordination isomery of these compounds for the creation of a new versatile building block for the binding of crown ether moieties. Here, we report the first example of the 1,3-*N*,*S*-coordination of crown ether-containing *N*-diisopropoxyphosphinyl-*N*′-(benzo-15-crown-5)-4′-yl-thiourea (**HL$^I$**)[21] towards $Ni^{II}$.

## Results and discussion

*N*-Phosphorylated thiourea **HL$^I$**, its non-crown ether-containing analog PhNHC(S)NHP(O)(O*i*Pr)$_2$ (**HL$^{II}_2$**) and complex **[NiL$^{II}_2$]** were prepared according to previously described methods.[21,24] Complex **[NiL$^I_2$]** was prepared by the following procedure: the ligand was converted into its lithium salt and subsequently reacted with Ni(NO$_3$)$_2$ in aqueous EtOH (Scheme 1). The reaction of **[NiL$^{I,II}_2$]** with 2,2′-bipyridine (**bipy**) and 1,10-phenanthroline (**phen**) in benzene lead to the formation of the heteroligand complexes **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]** (Scheme 2).

The compounds obtained were crystalline solids that were soluble in most polar solvents and insoluble in n-hexane.

The IR spectrum of **[NiL$^I_2$]** is typical of 1,3-*N*,*S*-chelate complexes of *N*-phosphoryl thioureas.[22,23] The band for the P=O group of the anionic ligand **L$^I$** is shifted by 16 cm$^{-1}$ to lower frequencies relative to the band of the parent ligand ($\nu_{P=O}$ 1250 cm$^{-1}$ for **HL$^I$**).[21] Thus, the frequency observed for the phosphoryl group band testifies to the absence of

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† CCDC reference numbers 732320 (**HL$^I$**), 732346 (**[NiL$^I_2$]**) and 735416 (**[Ni(bipy)L$^{II}_2$]**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00252a

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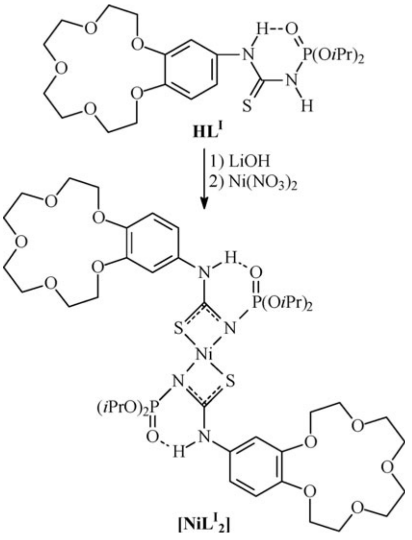
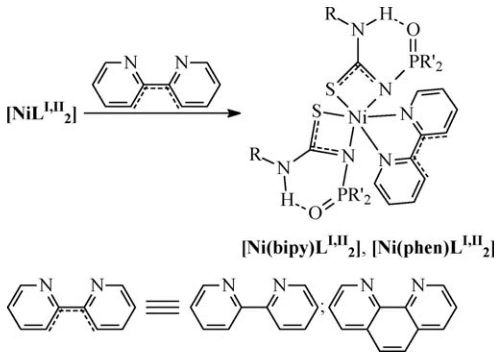


**Scheme 1** The preparation of **[NiL$^{I}_2$]**.



**Scheme 2** The preparation of **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]**. R = 4′-Benzo-15-crown-5, Ph. R′ = O*i*Pr.

coordination with the central ion.[23] A band at 3180 cm$^{-1}$ is observed for the NH group in the IR spectrum of **[NiL$^{I}_2$]** that is within the characteristic range for amide protons participating in hydrogen bonds.[20,22,23] There is a band at 1556 cm$^{-1}$ corresponding to the conjugated SCN fragment. Besides a very strong band for the POC group at 1016 cm$^{-1}$, there is a band for the COC group at 1135 cm$^{-1}$.

The IR spectra of **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]** are similar. The bands for the P═O and NH groups are at 1200–1237 and 3135–3160 cm$^{-1}$, respectively, and essentially at the same values as those observed for the parent complexes **[NiL$^{I,II}_2$]** ($\nu_{P=O}$ 1196 and $\nu_{NH}$ 3152 cm$^{-1}$ for **[NiL$^{II}_2$]**).[24] This testifies to the conservation of the coordination mode of the phosphorus-containing ligands. The band at 1532–1562 cm$^{-1}$ corresponds to the conjugated SCN fragment. The band for the POC group is observed at 998–1015 cm$^{-1}$. Besides these bands, a characteristic band for the COC group at 1114–1129 cm$^{-1}$ testifies to the preservation of the crown ethers in **[Ni(bipy)L$^{I}_2$]** and **[Ni(phen)L$^{I}_2$]**.

The $^{31}$P{$^{1}$H} NMR spectra of **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]** contain a signal at 2.0–2.5 ppm, slightly down-field-shifted relative to the parent complexes **[NiL$^{I,II}_2$]** ($\delta_P$ 1.7 ppm for **[NiL$^{II}_2$]**).[24]

In the $^{1}$H NMR spectra of **[NiL$^{I}_2$]**, **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]**, a pair of signals is observed for the *i*PrO protons. The signals for the methyl protons are observed at 1.03–1.65 ppm and the signals at 4.49–4.81 ppm correspond to the OCH protons. The $C_6H_3$, $C_6H_5$ and polyaromatic proton signals are observed at 6.76–8.80 ppm. The signals for the $CH_2$ protons of the crown ether fragment are in the range 3.57–4.37 ppm.

Only one NH proton signal is observed in the $^{1}$H NMR spectra of **[NiL$^{I}_2$]**, **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]**. The influence of the intramolecular hydrogen bond, in combination with deshielding effect of the aromatic group, result in a shift of this signal to 9.37–10.37 ppm.

Crystals of **HL$^{I}$**, **[NiL$^{I}_2$]** and **[Ni(bipy)L$^{II}_2$]** were obtained by slow evaporation of their corresponding solutions of a dichloromethane–n-hexane mixture, v/v 1 : 5 (Table 1).

The bond lengths in the *N*-thioacylamidophosphate moiety of **HL$^{I}$** are typical of *N*-phosphorylated thioureas and thioamides (Table 2).[20] The molecule in the crystal has a *syn*-orientation of the C1–S1 and C2–N2 bonds, and an *anti*-orientation of the C1–S1 and N1–P1 bonds (Fig. 1). The C1–S1 and P1–O1 bonds are in an *anti*-orientation. Such an arrangement is apparently caused by the formation of intramolecular N2–H2d···O1 hydrogen bridges and additional intermolecular N1–H1···O1_a bonds (Table 3). Also, as a result of the intermolecular interactions, a polymeric chain is formed (Fig. 2).

Complex **[NiL$^{I}_2$]** (Fig. 3) is centrosymmetric. The Ni$^{II}$ ion lies on a two-fold axis and is coordinated in a square-planar fashion, with the ligands arranged in a *trans*-configuration. The four-membered Ni–S–C–N metallocycles are flat. The endocyclic N–Ni–S angles in the four-membered rings fall in the range 74–75°. Inspection of the C═S and P–N bond lengths, and a comparison with those found in the parent ligand **HL$^{I}$**, indicate that these are best described as single bonds, while the P═O distance indicates the presence of a double bond (Table 2).[20,22–25]

The ArNH protons are engaged in intramolecular hydrogen bonds of the ArN–H···O═P type. Due to their formation, a flat *syn,syn*-conformation of the N–C–N–P–O unit is favored (Fig. 3) A similar pattern was also observed for **[NiL$^{II}_2$]**.[24]

An important feature of 1,3-*N*,*S*-chelate complexes in comparison with their 1,5-*O*,*S*- analogs is the ability to form intermolecular hydrogen bonds (Table 3), leading to polymeric chains (Fig. 4), and, in case of ligand **L$^{I}$**, to a close arrangement of the macrocyclic moieties in the crystal of **[NiL$^{I}_2$]**.

The distances between the opposite oxygen atoms are in the range 4.1–4.5 Å. This effect can be used for the creation of crystals with advanced set properties (*e.g.*, in the design of ion channels).

It is noteworthy that in the crystals of both **HL$^{I}$** and **[NiL$^{I}_2$]**, the crown ether moieties stack on top of each other; furthermore, the next-nearest molecules form two channels. The distances between two crown ether moieties within a channel corresponds to *ca.* 9.9 (the length of the *c*-axis) and 10.5 (the length of the *a*-axis) Å in **HL$^{I}$** and **[NiL$^{I}_2$]**, respectively. This phenomenon is not observed frequently. Similar stacked crown ether-containing compounds have been described by Fromm *et al.*[26–29]

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Published on 01 October 2009 on http://pubs.rsc.org | doi:10.1039/B9NJ00252A
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**Table 1** Crystal data and data collection details for **HL$^{\mathrm{I}}$**, **[NiL$^{\mathrm{I}}_2$]** and **[Ni(bipy)L$^{\mathrm{II}}_2$]**†

| | **HL$^{\mathrm{I}}$** | **[NiL$^{\mathrm{I}}_2$]** | **[Ni(bipy)L$^{\mathrm{II}}_2$]** |
|---|---|---|---|
| Empirical formula | $C_{21}H_{35}N_2O_8PS$ | $C_{42}H_{68}N_4NiO_{16}P_2S_2$ | $C_{36}H_{48}N_6NiO_6P_2S_2$ |
| Formula weight | 506.54 | 1069.77 | 845.57 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| Space group | *Cc* | *C*2/*c* | *Fdd*2 |
| $a$/Å | 31.721(19) | 10.4922(15) | 33.048(7) |
| $b$/Å | 8.715(5) | 15.482(3) | 27.265(5) |
| $c$/Å | 9.919(6) | 32.203(6) | 9.041(2) |
| $\beta$ (°) | 106.486(7) | 93.214(13) | — |
| $V$/Å$^3$ | 2629(3) | 5222.8(16) | 8147(3) |
| $Z$ | 4 | 4 | 8 |
| $D_{\mathrm{calc}}$/g cm$^{-3}$ | 1.280 | 1.360 | 1.379 |
| $T$/K | 296 | 293 | 153 |
| $F$(000) | 1080 | 2264 | 3552 |
| $\mu$/mm$^{-1}$ | 0.229 | 0.580 | 0.708 |
| Reflections collected | 7658 | 5562 | 19710 |
| Unique reflections | 4826 | 5266 | 4666 |
| Observed reflections | 3430 | 3106 | 3853 |
| | $R_{\mathrm{int}} = 0.023$ | $R_{\mathrm{int}} = 0.027$ | $R_{\mathrm{int}} = 0.097$ |
| $R$ indices (all data) | $R_1 = 0.0667$ | $R_1 = 0.0502$ | $R_1 = 0.0416$ |
| | w$R_2 = 0.1885$ | w$R_2 = 0.1403$ | w$R_2 = 0.0653$ |
| Flack parameter | 0.23(12) | | –0.005(11) |

**Table 2** Selected bond lengths (Å) and bond angles (°) for **HL$^{\mathrm{I}}$**, **[NiL$^{\mathrm{I–V}}_2$]** and **[Ni(bipy)L$^{\mathrm{II}}_2$]**

| | **HL$^{\mathrm{I}}$** | **[NiL$^{\mathrm{I}}_2$]** | **[NiL$^{\mathrm{II}}_2$]**$^{a,24}$ | | **[NiL$^{\mathrm{III}}_2$]**$^{b,23}$ | **[NiL$^{\mathrm{IV}}_2$]**$^{c,23}$ | **[NiL$^{\mathrm{V}}_2$]**$^{d,23}$ | | **[Ni(bipy)L$^{\mathrm{II}}_2$]** | |
|---|---|---|---|---|---|---|---|---|---|---|
| C═S | 1.673(5) | 1.739(3) | 1.732(3) | 1.737(3) | 1.713(4) | 1.725(3) | 1.716(3) | 1.741(3) | 1.705(3) | |
| P═O | 1.459(4) | 1.453(2) | 1.471(2) | | 1.475(3) | 1.482(2) | 1.460(2) | 1.476(2) | 1.479(2) | |
| P–N | 1.647(5) | 1.653(3) | 1.647(3) | 1.655(3) | 1.466(3) | 1.653(2) | 1.645(3) | 1.661(2) | 1.635(2) | |
| C–N(P) | 1.386(7) | 1.335(4) | 1.332(5) | 1.342(5) | 1.362(5) | 1.342(4) | 1.353(4) | 1.354(4) | 1.350(3) | |
| C–N(C) | 1.310(6) | 1.317(4) | 1.330(5) | 1.338(5) | 1.335(5) | 1.432(4) | 1.313(4) | 1.329(4) | 1.346(3) | |
| Ni–S | | 2.2047(10) | 2.2204(11) | 2.2208(11) | 2.2440(11) | 2.2277(9) | 2.2130(9) | 2.2190(13) | 2.4624(8) | |
| Ni–N | | | | | | | | | **LII** | **bipy** |
| Ni–N | | 1.903(2) | 1.906(3) | 1.907(3) | 1.912(3) | 1.909(2) | 1.895(3) | 1.896(2) | 2.106(2) | 2.075(2) |
| S–C–N(C) | 126.8(4) | 124.2(2) | 125.1(3) | 125.5(3) | 125.7(3) | 125.3(2) | 128.0(2) | 128.1(3) | 126.0(2) | |
| S–C–N(P) | 117.9(3) | 108.2(2) | 108.5(2) | 109.1(2) | 110.7(3) | 110.1(2) | 107.9(2) | 108.4(2) | 113.6(2) | |
| N–C–N | 115.3(4) | 127.6(3) | 125.8(3) | 126.0(3) | 123.6(4) | 124.6(3) | 123.7(3) | 123.9(3) | 120.5(2) | |
| C–N–P | 132.1(3) | 127.1(2) | 126.8(3) | 128.0(3) | 125.4(3) | 125.2(2) | 126.6(2) | 128.0(2) | 126.3(2) | |
| N–P–O | 110.5(2) | 111.36(14) | 111.5(2) | 113.2(2) | 108.3(2) | 112.82(13) | 111.5(2) | 112.43(13) | 114.21(10) | |
| N–Ni–S$_{endo}$ | | 74.59(8) | 74.36(9) | 74.50(9) | 74.75(11) | 74.75(8) | 74.04(9) | 75.19(9) | 67.75(5) | |
| Ni–S–C | | 77.63(11) | 77.21(13) | 77.43(13) | 76.81(14) | 76.84(11) | 77.34(11) | 78.10(13) | 78.33(9) | |
| | | | | | | | | | **LII** | **bipy** |
| Ni–N–C$_{endo}$ | | 99.5(2) | 99.3(2) | 99.4(2) | 97.8(3) | 98.3(2) | 99.1(2) | 99.9(2) | 100.26(15) | 114.65(15) |

$^a$ **HL$^{\mathrm{II}}$** = PhNHC(S)NP(O)(O*i*Pr)$_2$. $^b$ **HL$^{\mathrm{III}}$** = *p*-MeOC$_6$H$_4$NHC(S)NP(O)(O*i*Pr)$_2$. $^c$ **HL$^{\mathrm{IV}}$** = *p*-BrC$_6$H$_4$NHC(S)NP(O)(O*i*Pr)$_2$. $^d$ **HL$^{\mathrm{V}}$** = *t*BuNHC(S)NP(O)(O*i*Pr)$_2$; data for two independent molecules.

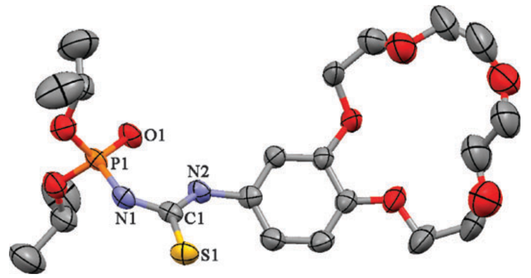

**Fig. 1** A thermal ellipsoid representation of **HL$^{\mathrm{I}}$** (C = grey, N = blue, O = red, P = orange, S = yellow). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

**Table 3** Hydrogen bond lengths (Å) and angles (°) for **HL$^{\mathrm{I}}$**, **[NiL$^{\mathrm{I}}_2$]** and **[Ni(bipy)L$^{\mathrm{II}}_2$]**

| | D–H···A | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|---|
| **HL$^{\mathrm{I}}$**$^a$ | N1–H1···O1_a$^{\#1}$ | 0.86 | 1.95 | 2.792(5) | 166 |
| | N2–H2···O1 | 0.86 | 1.96 | 2.732(6) | 150 |
| **[NiL$^{\mathrm{I}}_2$]**$^b$ | N2–H2···O1 | 0.86 | 2.20 | 2.851(4) | 132 |
| | N2–H2···O1_a$^{\#1}$ | 0.86 | 2.10 | 2.847(3) | 144 |
| **[Ni(bipy)L$^{\mathrm{II}}_2$]**$^c$ | N2–H2···O1 | 0.88 | 1.90 | 2.695(3) | 149 |
| | C7–H7···S1 | 0.95 | 2.54 | 3.228(3) | 129 |
| | C9–H9···S1$^{\#1}$ | 0.95 | 2.80 | 3.524(3) | 133 |
| | C11–H11···O1$^{\#2}$ | 0.95 | 2.30 | 3.226(3) | 166 |
| | C12–H12···S1 | 0.95 | 2.78 | 3.394(3) | 123 |
| | C13–H13···O1 | 1.00 | 2.57 | 2.955(3) | 103 |
| | C18–H18_a···O1 | 0.98 | 2.52 | 3.213(4) | 128 |

$^a$ Symmetry code #1: $x$, $1 - y$, $-\frac{1}{2} + z$. $^b$ Symmetry code #1: $-x$, $y$, $\frac{1}{2} - z$. $^c$ Symmetry code #1: $\frac{1}{4} + x$, $\frac{3}{4} - y$, $-\frac{1}{4} + z$; #2: $x$, $y$, $-1 + z$.

According to the X-ray data, complex **[Ni(bipy)L$^{\mathrm{II}}_2$]** contains a distorted trigonal-antiprismatic NiN$_4$S$_2$ core (Fig. 5), the P–N and C═S bond lengths are shortened, and the C–N(C) and P═O distances are lengthened (Table 2) in comparison with the corresponding interatomic distances reported for **[NiL$^{\mathrm{II}}_2$]**.[24] The C–N(P) distances are essentially similar in both complexes **[NiL$^{\mathrm{II}}_2$]** and **[Ni(bipy)L$^{\mathrm{II}}_2$]**. The Ni–S

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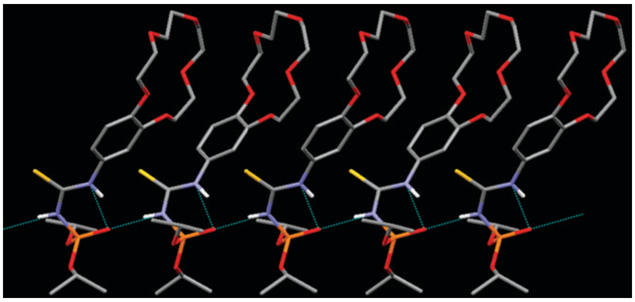

**Fig. 2** The crystal packing of **HL$^{I}$** (C = grey, H = white, N = blue, O = red, P = orange, S = yellow). Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

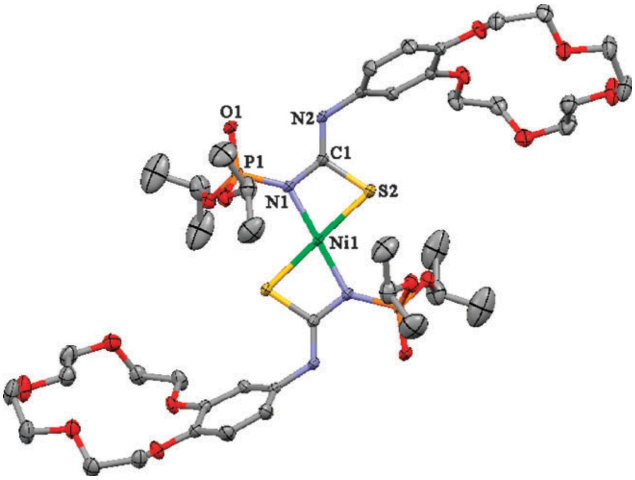

**Fig. 3** A thermal ellipsoid representation of **[NiL$^{I}_{2}$]** (C = grey, N = blue, Ni = green, O = red, P = orange, S = yellow). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

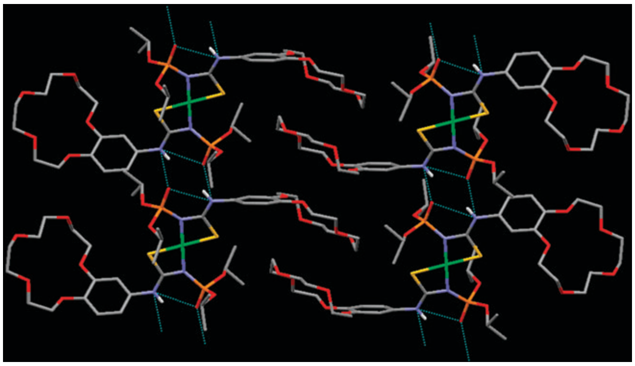

**Fig. 4** The crystal packing of **[NiL$^{I}_{2}$]** (C = grey, H = white, N = blue, Ni = green, O = red, P = orange, S = yellow). H-atoms, not involved in hydrogen bonding are omitted for clarity.

and Ni–N bond lengths for **[Ni(bipy)L$^{II}_{2}$]** are significantly lengthened, and the N–Ni–S$_{endo}$ angles are smaller compared to the parent complex. This is due to the presence of the additional donor ligand. The four-membered Ni–S–C–N metallocycles are flat. The five-membered Ni–N–C–C–N metallocycle is slightly distorted with a torsion angle N3–C8–C8_a–N3_a of −7.3(3)°.

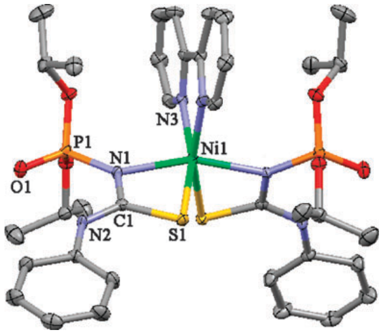

**Fig. 5** A thermal ellipsoid representation of **[Ni(bipy)L$^{II}_{2}$]** (C = grey, N = blue, Ni = green, O = red, P = orange, S = yellow). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

There are intramolecular N–H···O=P hydrogen bonds in the crystal of **[Ni(bipy)L$^{II}_{2}$]** (Fig. 6, Table 3) that are formed between the hydrogen atoms of the NH groups and the oxygen atoms of the P=O groups of the anionic ligands. There are also intermolecular C–H···O=P and C–H···S=C hydrogen bonds (Fig. 6, Table 3). These bonds are formed between the two hydrogen atoms of the bipyridine ligand of one molecule, and the P=O oxygen atoms and C=S sulfur atoms of three neighboring molecules, while the P=O oxygen atoms and the C=S sulfur atoms of the same molecule also form hydrogen bonds with the bipyridine hydrogen atoms of a further three neighboring molecules (Fig. 6).

Thus, a 3D network of hydrogen bridges is found in the crystal of **[Ni(bipy)L$^{II}_{2}$]**, highlighting the importance of hydrogen bonding for stabilizing the 1,3-*N*,*S*-isomer and forming a supramolecular network in the crystal phase.

Compounds **HL$^{I}$**, **[NiL$^{I}_{2}$]**, **[Ni(bipy)L$^{I}_{2}$]** and **[Ni(phen)L$^{I}_{2}$]** contain a set of active nucleophilic (crown ether and phosphoryl group oxygen atoms) and electrophilic sites (tetracoordinated Ni$^{II}$ cation in **[NiL$^{I}_{2}$]**). This makes them interesting as new building blocks for supramolecular structures.

An investigation of the extraction properties of **HL$^{I}$**, **[NiL$^{I}_{2}$]**, **[Ni(bipy)L$^{I}_{2}$]** and **[Ni(phen)L$^{I}_{2}$]** towards alkali metal picrates, in comparison with 4′-aminobenzo-15-crown-5 (**1**), benzo-15-crown-5 (**2**) and 18-crown-6 (**3**), were performed (Table 4). It is noteworthy that the extraction properties of **[NiL$^{I}_{2}$]**, **[Ni(bipy)L$^{I}_{2}$]** and **[Ni(phen)L$^{I}_{2}$]** did not depend on the $M^{+}Pic^{-}$ to crown ether-containing compound molar ratio.

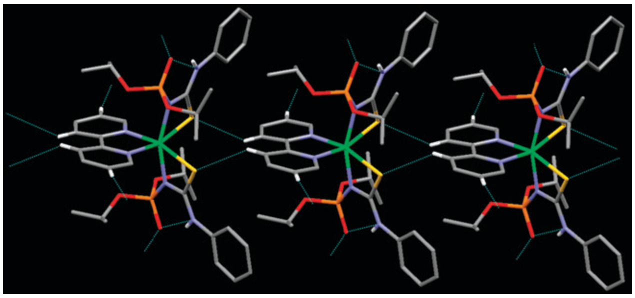

**Fig. 6** The crystal packing of **[Ni(bipy)L$^{II}_{2}$]** (C = grey, H = white, N = blue, Ni = green, O = red, P = orange, S = yellow). Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

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**Table 4** The extraction properties of crown ether-containing compounds **HL$^I$**, **[NiL$^I_2$]**, **[Ni(bipy)L$^I_2$]** and **[Ni(phen)L$^I_2$]** towards alkali metal picrates ($M^+Pic^-$) in a $CH_2Cl_2/H_2O$ medium

| | $Li^+$ | $Na^+$ | $K^+$ | $NH_4^+$ |
|---|---|---|---|---|
| **HL$^I$** | 1.0 | 14.9 | 12.3 | 37.2 |
| **[NiL$^I_2$]**$^a$ | 2.8/2.0 | 83.4/81.2 | 7.1/5.7 | 10.7/9.1 |
| **[Ni(bipy)L$^I_2$]**$^a$ | 0.4/0.6 | 11.7/10.9 | 5.2/4.4 | 21.3/20.7 |
| **[Ni(phen)L$^I_2$]**$^a$ | 0.5/0.3 | 8.3/9.0 | 6.5/5.8 | 24.0/24.6 |
| **1** | 2.6 | 1.3 | 5.6 | 35.2 |
| **2** | 2.6 | 5.1 | 9.9 | 24.2 |
| **3** | 9.7 | 13.6 | 62.5 | 61.3 |

$^a$ $M^+Pic^-$ to crown ether-containing compound molar ratio 1 : 1/2 : 1.

This indicates that both crown ethers of the molecules interact with $M^+Pic^-$.

From our experiments, it is evident that **[NiL$^I_2$]** expresses an affinity towards the $Na^+$ cation compared with parent ligand **HL$^I$** and crown ethers **1–3**. Such dramatic selectivity changes might be explained by the assistance of the donor centers of the exocyclic chelate moieties and a change in the hydrophilic/hydrophobic balance caused by the bulky organometallic substituents. A decrease of the $Na^+$ extraction capacity was observed for **[Ni(bipy)L$^I_2$]** and **[Ni(phen)L$^I_2$]** compared to **[NiL$^I_2$]**, which might be due to steric hindrance. In contrast, the $NH_4^+$ extraction increased going from **[NiL$^I_2$]** to hexacoordinated complexes, which could be explained by the lability of the ammonium cation.

## Conclusions

In summary, the data presented confirms that the formation of intramolecular N–H···O=P hydrogen bonds is a necessary condition for 1,3-*N*,*S*-isomer stabilization in a square-planar Ni$^{II}$ complex with *N*-phosphorylated thiourea containing a crown ether fragment. Conservation of the coordination mode of deprotonated ligands **L$^{I,II}$** was observed in heteroligand complexes **[Ni(bipy)L$^{I,II}_2$]** and **[Ni(phen)L$^{I,II}_2$]**.

The complex **[NiL$^I_2$]** showed an increase in $Na^+$ extraction capacity compared with the other crown ether-containing complexes described above.

## Experimental

### General procedures

Infrared spectra (Nujol) were recorded using a Specord M-80 spectrometer in the range 400–3600 cm$^{-1}$. NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. $^1$H and $^{31}$P{$^1$H} NMR spectra ($CDCl_3$) were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ ($^1$H) and $H_3PO_4$ ($^{31}$P{$^1$H}). Electronic absorption spectra were recorded in the range 250–400 nm on a Perkin-Elmer Lambda 35 spectrophotometer. Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer.

### Syntheses

**HL$^{I,II}$.** *N*-Phosphorylated thioureas were prepared according to previously described methods.[21,24]

**[NiL$^{II}_2$].** This complex was prepared according to a previously described method.[24]

**[NiL$^I_2$].** A suspension of **HL$^I$** (0.253 g, 0.5 mmol) in aqueous ethanol (35 mL) was mixed with an ethanolic solution of lithium hydroxide (0.013 g, 0.55 mmol). An aqueous (20 mL) solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.087 g, 0.3 mmol) was added dropwise with vigorous stirring. The reaction mixture was stirred at room temperature for a further 5 h. Next, the resulting complex was extracted using dichloromethane. The combined extracts were washed with water and dried using anhydrous $MgSO_4$. The solvent was then removed under vacuum. A precipitate was isolated by adding n-hexane to a dichloromethane solution of the residue. Yield: 0.115 g (43%). Mp. 179–180 °C. $^1$H NMR: 1.38 (d, $^3J_{H,H}$ = 5.4 Hz, 12 H, $CH_3$), 1.65 (d, $^3J_{H,H}$ = 5.4 Hz, 12 H, $CH_3$), 3.63–4.25 (m, 32 H, $CH_2$, crown), 4.54–4.75 (m, 4 H, OCH), 6.76–7.03 (m, 6 H, $C_6H_3$) and 10.37 (s, 2 H, NH) ppm. $^{31}$P{$^1$H} NMR: 1.9 ppm. IR: $\nu$ 995 (POC), 1135 (COC), 1234 (P=O), 1515, 1556 (SCN) and 3168 (NH) cm$^{-1}$. $C_{42}H_{68}N_4NiO_{16}P_2S_2$ (1068.29): calc. C, 47.15; H, 6.41; N, 5.24. Found C, 47.33; H, 6.43; N, 5.13%.

**[Ni(bipy)L$^{I,II}_2$] and [Ni(phen)L$^{I,II}_2$].** A solution of complexes **[NiL$^I_2$]** (0.107, 0.1 mmol) or **[NiL$^{II}_2$]** (0.069 g, 0.1 mmol) in benzene (10 mL) was added dropwise to a stirred solution of 2,2′-bipyridine (0.016 g, 0.1 mmol) or 1,10-phenanthroline (0.018 g, 0.1 mmol) in benzene (10 mL). After complete addition, the solution was stirred for one hour. The solvent was then removed under vacuum. The residue was recrystallized from a dichloromethane/n-hexane mixture.

**[Ni(bipy)L$^I_2$].** Yield: 0.103 g (84%). Mp. 128–131 °C. $^1$H NMR: 1.14–1.37 (m, 24 H, $CH_3$), 3.57–4.08 (m, 32 H, $CH_2$, crown), 4.49–4.68 (m, 4 H, OCH), 6.81–8.74 (m, $C_6H_3$ + bipy, overlapped with solvent signal) and 9.73 (s, 2 H, NH) ppm. $^{31}$P{$^1$H} NMR: 2.3 ppm. IR: $\nu$ 1004 (POC), 1129 (COC), 1229 (P=O), 1547 (SCN) and 3160 (NH) cm$^{-1}$. $C_{52}H_{76}N_6NiO_{16}P_2S_2$ (1225.96): calc. C, 50.95; H, 6.25; N, 6.86. Found C, 50.82; H, 6.37; N, 6.71%.

**[Ni(phen)L$^I_2$].** Yield: 0.114 g (91%). Mp. 143–144 °C. $^1$H NMR: 1.03–1.28 (m, 24 H, $CH_3$), 3.68–4.37 (m, 32 H, $CH_2$, crown), 4.59–4.81 (m, 4 H, OCH), 6.93–8.59 (m, $C_6H_3$ + phen, overlapped with solvent signal) and 9.59 (s, 2 H, NH) ppm. $^{31}$P{$^1$H} NMR: 2.5 ppm. IR: $\nu$ 1015 (POC), 1114 (COC), 1237 (P=O), 1532 (SCN) and 3152 (NH) cm$^{-1}$. $C_{54}H_{76}N_6NiO_{16}P_2S_2$ (1249.99): calc. C, 51.89; H, 6.13; N, 6.72. Found C, 52.05; H, 6.26; N, 6.59%.

**[Ni(bipy)L$^{II}_2$].** Yield: 0.079 g (94%). Mp. 130–132 °C. $^1$H NMR: 1.21–1.48 (m, 24 H, $CH_3$), 4.59–4.80 (m, 4 H, OCH), 7.28–8.80 (m, 18 H, Ph + bipy) and 9.52 (s, 2 H, NH) ppm. $^{31}$P{$^1$H} NMR: 2.0 ppm. IR: $\nu$ 1008 (POC), 1200 (P=O), 1562 (SCN) and 3135 (NH) cm$^{-1}$. $C_{36}H_{48}N_6NiO_6P_2S_2$ (845.57): calc. C, 51.14; H, 5.72; N, 9.94. Found C, 51.03; H, 5.69; N, 10.02%.

**[Ni(phen)L$^{II}_2$].** Yield: 0.076 g (87%). Mp. 164–166 °C. $^1$H NMR: 1.15–1.36 (m, 24 H, $CH_3$), 4.51–4.84 (m, 4 H, OCH), 7.19–8.74 (m, 18 H, Ph + phen) and 9.37 (s, 2 H, NH) ppm.

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$^{31}P\{^1H\}$ NMR: 2.4 ppm. IR: $\nu$ 998 (POC), 1202 (P=O), 1540 (SCN) and 3142 (NH) cm$^{-1}$. $C_{38}H_{48}N_6NiO_6P_2S_2$ (869.59): calc. C, 52.49; H, 5.56; N, 9.66. Found C, 52.64; H, 5.42; N, 9.79%.

### Picrate extraction experiment

Single-species lithium, sodium, potassium or ammonium picrate extraction was conducted with 3 mL of an aqueous solution containing 100 mM of LiOH, NaOH, KOH or $NH_4SCN$ and 0.07 mM of picric acid, and 3 mL of a 0.07 mM $CH_2Cl_2$ solution of **[NiL$^I_2$]**, **[Ni(bipy)L$^I_2$]**, **[Ni(phen)L$^I_2$]**, **1**, **2** or **3**. The resulting mixture was stirred for 5 h and left for a further one hour for layer separation. The degree of extraction was calculated from the difference of the absorption of the initial cation picrate solution ($\lambda$ = 374 nm) and the separated aqueous layer.

### X-Ray crystallography†

Data for **HL$^I$** and **[NiL$^I_2$]** were collected on a Bruker SMART Apex2 CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda$ = 0.71073 Å). The images were indexed, integrated and scaled using the APEX2 data reduction package.[30] All raw data were corrected for absorption using the SADABS[31] program. The structures were solved by direct methods using the SIR[32] program and refinement was carried out using SHELXL-97[33] using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were added to the structure model in calculated positions and were refined as rigid atoms. All calculations were performed on a personal computer using the WinGX program.[34]

Diffraction data for **[Ni(bipy)L$^{II}_2$]** were collected on a Bruker AXS APEX CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda$ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Data reduction was performed using the Bruker SMART[30] program package. Structure solutions were found using the SHELXS-97[33] package by the heavy atom method or by direct methods, and were refined using SHELXL-97[33] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were added to the structure models in calculated positions. The molecule resides on a two-fold axis.

## Acknowledgements

This work was supported by the Russian Science Support Foundation. D. A. S. and M. G. B. thank DAAD for scholarships (Forschungsstipendien 2008/2009).

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