The influence of an intramolecular hydrogen bond on the 1,3-N,Scoordination of crown ether-containing N-phosphorylthiourea with Ni^{II}[†]

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Reaction of the lithium salt of *N*-phosphorylated thiourea [4'-benzo-15-crown-5]-NHC(S)NHP(O)(O*i*Pr)₂ (HL¹) with Ni^{II} leads to the chelate complex [NiL¹₂]. The metal center is found in a square-planar N₂S₂ environment formed by the C=S sulfur atoms and the P–N nitrogen atoms of two deprotonated L¹ ligands. Reaction of [NiL¹₂] 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^I₂] 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 cations²¹ 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)(OiP_1)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 d⁸ [M{RN(H)C(S)NP(O)(OiP_1)₂-*N*,*S*}₂] complexes and (ii) the formation of strong (20–25 kJ mol⁻¹)²² intra-molecular 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 (\mathbf{HL}^{I})²¹ towards Ni^{II}.

Results and discussion

N-Phosphorylated thiourea \mathbf{HL}^{I} , its non-crown ether-containing analog PhNHC(S)NHP(O)(O $(Pr)_2$ (\mathbf{HL}^{II}_2) and complex [Ni \mathbf{L}^{II}_2] were prepared according to previously described methods.^{21,24} Complex [Ni \mathbf{L}^{I}_2] was prepared by the following procedure: the ligand was converted into its lithium salt and subsequently reacted with Ni(NO₃)₂ in aqueous EtOH (Scheme 1). The reaction of [Ni $\mathbf{L}^{I,II}_2$] with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) in benzene lead to the formation of the heteroligand complexes [Ni(bipy) $\mathbf{L}^{I,II}_2$] and [Ni(phen) $\mathbf{L}^{I,II}_2$] (Scheme 2).

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

The IR spectrum of $[NiL_2^I]$ 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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Scheme 1 The preparation of [NiL¹₂].



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 $[NiL_2]$ 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 ν_{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 ³¹P{¹H} 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 $[NiL^{I,II}_2]$ (δ_P 1.7 ppm for $[NiL^{II}_2]$).²⁴

In the ¹H NMR spectra of $[NiL_2]$, $[Ni(bipy)L_2]$ and $[Ni(phen)L_2]$, 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 C₆H₃, C₆H₅ and polyaromatic proton signals are observed at 6.76–8.80 ppm. The signals for the CH₂ protons of the crown ether fragment are in the range 3.57–4.37 ppm.

Only one NH proton signal is observed in the ¹H NMR spectra of [NiL¹₂], [Ni(bipy)L^{1,II}₂] and [Ni(phen)L^{1,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 $[NiL_2^1]$ (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 $[NiL_{2}]^{.24}$

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 [NiL¹₂].

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 $[NiL_{2}^{I}]$, 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 $[NiL_{2}^{I}]$, 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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Table 1 Crystal data and data collection details for HL ¹ , [NiL ¹ ₂] and [Ni(bipy)]	¹¹ ₂	ŀ	ŀ	
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	HL ^I	[NiL ¹ ₂]	[Ni(bipy)L ^{II} 2]
Empirical formula	C ₂₁ H ₃₅ N ₂ O ₈ PS	C42H68N4NiO16P2S2	C ₃₆ H ₄₈ N ₆ NiO ₆ P ₂ S ₂
Formula weight	506.54	1069.77	845.57
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	Cc	C2/c	Fdd2
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)
β (°)	106.486(7)	93.214(13)	
$V/Å^3$	2629(3)	5222.8(16)	8147(3)
Z	4	4	8
$D_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.280	1.360	1.379
T/K	296	293	153
F(000)	1080	2264	3552
μ/mm^{-1}	0.229	0.580	0.708
Reflections collected	7658	5562	19710
Unique reflections	4826	5266	4666
Observed reflections	3430	3106	3853
	$R_{\rm int} = 0.023$	$R_{\rm int} = 0.027$	$R_{\rm int} = 0.097$
R indices (all data)	$R_1 = 0.0667$	$R_1 = 0.0502$	$R_1 = 0.0416$
	$wR_2 = 0.1885$	$wR_2 = 0.1403$	$WR_2 = 0.0653$
Flack parameter	0.23(12)		-0.005(11)

 $Table \ 2 \quad Selected \ bond \ lengths (\mathring{A}) \ and \ bond \ angles (^{\circ}) \ for \ HL^{I}, \ [NiL^{I-V}{}_{2}] \ and \ [Ni(bipy)L^{II}{}_{2}]$

	HLI	[NiL ^I ₂]	[NiL ¹	1 ₂] ^{<i>a</i>,24}	$[NiL^{III}_2]^{b,23}$	[NiL ^{IV} ₂] ^{c,23}	[NiL	v ₂] ^{d,23}	[Ni(bip	y)L ^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-Sendo		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-Cendo		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 ^{II} = P	^{<i>a</i>} $\mathbf{HL^{II}} = PhNHC(S)NP(O)(OiPr)_2$. ^{<i>b</i>} $\mathbf{HL^{III}} = p-MeOC_6H_4NHC(S)NP(O)(OiPr)_2$. ^{<i>c</i>} $\mathbf{HL^{IV}} = p-BrC_6H_4NHC(S)NP(O)(OiPr)_2$. ^{<i>d</i>} $\mathbf{HL^{V}} = p-BrC_6H_4NHC(S)NP(O)(OiPr)_2$. ^{<i>d</i>} $\mathbf{HL^{V}} = p-BrC_6H_4NHC(S)NP(O)(OiPr)_2$.									
tBuNHC(S)N	P(O)(OiPr)2; data for tw	vo independer	nt molecules.						



Fig. 1 A thermal ellipsoid representation of HL^{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.

According to the X-ray data, complex $[Ni(bipy)L^{II}_2]$ contains a distorted trigonal-antiprismatic NiN₄S₂ 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

Table 3 Hydrogen bond lengths (Å) and angles (°) for $HL^{I},~[NiL^{I}_{2}]$ and $[Ni(bipy)L^{II}_{2}]$

	$D – H \cdots A$	D–H	H···A	D···A	D−H···A			
HL ^{Ia}	N1–H1···O1 a ^{#1}	0.86	1.95	2.792(5)	166			
	$N2-H2 \cdot \cdot \cdot O1$	0.86	1.96	2.732(6)	150			
$[NiL_2]^b$	N2-H2···O1	0.86	2.20	2.851(4)	132			
	N2–H2···O1 $a^{\#1}$	0.86	2.10	2.847(3)	144			
$[Ni(bipy)L^{II}_2]^c$	$N2-H2 \cdot \cdot \cdot O1$	0.88	1.90	2.695(3)	149			
	C7-H7···S1	0.95	2.54	3.228(3)	129			
	$C9-H9 \cdot \cdot \cdot S1^{\#1}$	0.95	2.80	3.524(3)	133			
	$C11-H11O1^{#2}$	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			
	$C18H18_a\text{-}\cdot\cdot\text{O}1$	0.98	2.52	3.213(4)	128			
^{<i>a</i>} Symmetry code #1: x , $1 - y$, $-\frac{1}{2} + z$. ^{<i>b</i>} Symmetry code #1: $-x$, y ,								
$\frac{1}{2} - z$. ^c Symmetry	etry code #1: $\frac{1}{4} + x$	$x^{3}, \frac{3}{4} - y$	$, -\frac{1}{4} + 2$	z; #2: x, y	, -1 + z.			

reported for $[NiL^{II}_{2}]^{.24}$ The C–N(P) distances are essentially similar in both complexes $[NiL^{II}_{2}]$ and $[Ni(bipy)L^{II}_{2}]$. The Ni–S



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 $[NiL_2^1]$ (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 $[NiL_2^1]$ (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 $-7.3(3)^{\circ}$.



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} , [NiL¹₂], [Ni(bipy)L¹₂] and [Ni(phen)L¹₂] 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 [NiL¹₂], [Ni(bipy)L¹₂] and [Ni(phen)L¹₂] 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.

Table 4	The extra	action prop	perties of	crown	ether-co	ontaining	com-
pounds 1	HL ^I , [NiL ^I	2], [Ni(bip	y)L ¹ ₂] and	1 [Ni(ph	$en)L_{2}^{I}$	towards	alkali
metal pic	crates (M ⁺	Pic ⁻) in a	CH_2Cl_2/H	I ₂ O me	dium		

	Li ⁺	Na ⁺	\mathbf{K}^+	$\mathrm{NH_4}^+$
HLI	1.0	14.9	12.3	37.2
$[NiL_{2}]^{a}$	2.8/2.0	83.4/81.2	7.1/5.7	10.7/9.1
$[Ni(bipy)L_2]^a$	0.4/0.6	11.7/10.9	5.2/4.4	21.3/20.7
$[Ni(phen)L_2]^a$	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 cro	wn ether-con	taining compou	and molar rat	tio $1:1/2:1$.

This indicates that both crown ethers of the molecules interact with $M^{\,+}\text{Pic}^{\,-}.$

From our experiments, it is evident that $[NiL_2^{I}]$ 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 $[Ni(bipy)L_2^{I}]$ and $[Ni(phen)L_2^{I}]$ compared to $[NiL_2^{I}]$, which might be due to steric hindrance. In contrast, the NH₄⁺ extraction increased going from $[NiL_2^{I}]$ 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 $[NiL_2]$ 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. ¹H and ³¹P{¹H} NMR spectra (CDCl₃) were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and H₃PO₄ (³¹P{¹H}). 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^I₂]. 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(NO₃)₂·6H₂O (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 MgSO₄. 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. ¹H NMR: 1.38 (d, ${}^{3}J_{H,H} = 5.4$ Hz, 12 H, CH₃), 1.65 (d, ${}^{3}J_{H,H} = 5.4$ Hz, 12 H, CH₃), 3.63–4.25 (m, 32 H, CH₂, 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. ³¹P{¹H} NMR: 1.9 ppm. IR: ν 995 (POC), 1135 (COC), 1234 (P=O), 1515, 1556 (SCN) and 3168 (NH) cm⁻¹. C₄₂H₆₈N₄NiO₁₆P₂S₂ (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^I₂] (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)L¹₂]. Yield: 0.103 g (84%). Mp. 128–131 °C. ¹H NMR: 1.14–1.37 (m, 24 H, CH₃), 3.57–4.08 (m, 32 H, CH₂, crown), 4.49–4.68 (m, 4 H, OCH), 6.81–8.74 (m, C₆H₃ + bipy, overlapped with solvent signal) and 9.73 (s, 2 H, NH) ppm. ³¹P{¹H} NMR: 2.3 ppm. IR: ν 1004 (POC), 1129 (COC), 1229 (P=O), 1547 (SCN) and 3160 (NH) cm⁻¹. C₅₂H₇₆N₆NiO₁₆P₂S₂ (1225.96): calc. C, 50.95; H, 6.25; N, 6.86. Found C, 50.82; H, 6.37; N, 6.71%.

[Ni(phen)L¹₂]. Yield: 0.114 g (91%). Mp. 143–144 °C. ¹H NMR: 1.03–1.28 (m, 24 H, CH₃), 3.68–4.37 (m, 32 H, CH₂, crown), 4.59–4.81 (m, 4 H, OCH), 6.93–8.59 (m, C₆H₃ + phen, overlapped with solvent signal) and 9.59 (s, 2 H, NH) ppm. ³¹P{¹H} NMR: 2.5 ppm. IR: ν 1015 (POC), 1114 (COC), 1237 (P=O), 1532 (SCN) and 3152 (NH) cm⁻¹. C₅₄H₇₆N₆NiO₁₆P₂S₂ (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}_{2I} **].** Yield: 0.079 g (94%). Mp. 130–132 °C. ¹H NMR: 1.21–1.48 (m, 24 H, CH₃), 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. ³¹P{¹H} NMR: 2.0 ppm. IR: ν 1008 (POC), 1200 (P=O), 1562 (SCN) and 3135 (NH) cm⁻¹. C₃₆H₄₈N₆NiO₆P₂S₂ (845.57): cale. C, 51.14; H, 5.72; N, 9.94. Found C, 51.03; H, 5.69; N, 10.02%.

[Ni(phen) L^{H}_{2} **].** Yield: 0.076 g (87%). Mp. 164–166 °C. ¹H NMR: 1.15–1.36 (m, 24 H, CH₃), 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.

³¹P{¹H} NMR: 2.4 ppm. IR: ν 998 (POC), 1202 (P=O), 1540 (SCN) and 3142 (NH) cm⁻¹. C₃₈H₄₈N₆NiO₆P₂S₂ (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 NH₄SCN and 0.07 mM of picric acid, and 3 mL of a 0.07 mM CH₂Cl₂ solution of [NiL¹₂], [Ni(bipy)L¹₂], [Ni(phen)L¹₂], 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 $[NiL_{2}^{I}]$ were collected on a Bruker SMART Apex2 CCD diffractometer with graphite-monochromated Mo-K_{α} 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 SADABS³¹ program. The structures were solved by direct methods using the SIR³² program and refinement was carried out using SHELXL-97³³ 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 graphitemonochromated 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 SMART³⁰ program package. Structure solutions were found using the SHELXS-97³³ package by the heavy atom method or by direct methods, and were refined using SHELXL-97³³ 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.

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