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N-(Diisopropylthiophosphoryl)-N'-(R)-thioureas: synthesis, characterization, crystal structures and competitive bulk liquid membrane transport of some metal ions[†]

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Ten *N*-thiophosphorylated thioureas of the common formula RC(S)NHP(S)(O*i*Pr)₂ [R = *i*PrNH (1), EtNH (2), Et₂N (3), 2,5-Me₂C₆H₃NH (4), 4-Me₂NC₆H₄NH (5), 2-MeO(O)CC₆H₄NH (6), 2-PyNH (7), 2-PyCH₂NH (8), 3-PyCH₂NH (9), *cyclo*-C₂H₂N₃NH (10)] have been synthesized and characterized by IR, NMR spectroscopy and elemental analysis. Molecular structures of 1 and 4–8 were elucidated by X-ray diffraction revealing linear, bi- or trifurcated intramolecular hydrogen bonds. Additionally, their crystal structures are stabillized by two intermolecular hydrogen bonds, which in turn lead to a centrosymmetric dimer formation. The hydrogen bonded dimers of 5–8 are packed to polymeric chains through the $\pi \cdots \pi$ stacking interactions between aryl or pyridyl rings. Competitive transport experiments involving metal ions from an aqueous source phase through a chloroform membrane into an aqueous receiving phase have been carried out using 2–6 and 8–10 as the ionophore present in the organic phase. The source phase contained equimolar concentrations of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Ag^I, Cd^{II} and Pb^{II} with the source and receiving phases being buffered at pH = 5.5 and 1.0, respectively. The obtained data were compared with the transport and extraction properties of 1 and 7, which were described recently.

Introduction

Crystal engineering¹ is a main objective for the creation and design of new materials with desirable structures and properties. Understanding of intermolecular interactions and packing in crystals is one of the main goals for the fine tuning of a number of useful properties. Noncovalent interactions are considered as the most effective tool for the creation of molecular aggregates and assemblies.^{1,2} Among these interactions hydrogen bonds and $\pi \cdots \pi$ stacking are the most frequently used and legally take front rank due to their ability for rational design.³ The single crystal growth issue, which is mostly influenced by fortune than skills, can however be overcome by combination of donor and acceptor functions in a molecule providing an effective way for the formation of intra- and intermolecular interactions. In this frame, the (thio)urea group is frequently used as a crystallizing building block since it contains both hydrogen donors through the NH groups and acceptor centres through the C=O or C=S groups.⁴ The possibility to modify (thio)urea at will, with a wide

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range of functional groups at the nitrogen atoms, makes these molecules very attractive.

We have extensively studied the synthesis, membrane transport, extraction, separation and complexation properties of *N*-(thio)phosphorylated thioureas RR'NC(X)NHP(Y)(O*i*Pr)₂ (X, Y = O, S) (NTTU).⁵ The easiest synthetic way of NTTU is the reaction of primary or secondary amines with the corresponding (thio)phosphorylated isocyanates (*i*PrO)₂P(Y)NCX (X, Y = O, S).^{5*a*} The main advantageous of this synthetic route is the ability to work with molecules having one or more amine groups as a starting amine. Depending on the nature of the donor C=X and P=Y atoms, as well as on the presence of the NH fragment at the (thio)carbonyl group, a number of hydrogen bonded structures were observed in crystals of NTTU.^{5*a*} The influence of the R and R' substituents is also crucial for the formation of assemblies in crystals. Thus, investigation of NTTU is an outstanding and evergrowing branch of crystal engineering.

Herein, we report ten *N*-thiophosphorylated thioureas, containing various substituents at the thiocarbonyl group (Chart 1) with their IR and NMR data. The crystal structures and packing of 1 and **4–8** were elucidated by X-ray diffraction. The thioureas **3** and **7** were recently synthesized by two of us.⁶ However, in the present work we describe the crystal structure of **7**. Furthermore, the IR and NMR data of **3** were previously analyzed but not correctly interpreted.^{6b}

In this contribution we also studied the competitive bulk liquid membrane transport of some metal ions using **2–6** and **8–10**. We used the three phase arrangement, which involves two

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Chart 1

buffered aqueous phases (source and receiving phases) separated by an immiscible organic phase (chloroform) incorporating the ionophore.^{5c,d} The advantage of this procedure is a measurement (by difference) of metal ions present in the organic phase. The source phase contained equimolar concentrations of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Ag^I, Cd^{II} and Pb^{II}. The obtained data were compared with the transport properties of **1** and **7**, which were described recently.^{5c,d}

Results and discussion

The *N*-thiophosphorylated thioureas **1–10** were synthesized by reacting the corresponding amine with the isothiocyanate $(iPrO)_2P(S)NCS$. It is noteworthy, that according to the IR, NMR spectroscopy and elemental analysis (see below and Experimental section) the reaction of diethylamine with $(iPrO)_2P(S)NCS$ leads to the corresponding diethylammonium salt **3**·Et₂NH. The compounds **1** and **4–8** are colorless crystalline solids, whereas **2**, **3**·Et₂NH, **9** and **10** are yellow viscous oils. All compounds are soluble in dichloromethane, chloroform, acetone, acetonitrile and insoluble in n-hexane and water.

The IR spectra of 1, 2 and 4–10 contain a band at $632-647 \text{ cm}^{-1}$ for the P=S group. This band is shifted to low frequencies in the spectrum of $3 \cdot \text{Et}_2\text{NH}$ (at 617 cm⁻¹) and testifies of the presence of the anionic form of the thiophosphorylated thiourea 3. In the IR spectra of 1, 2 and 4–10 there is a band at 1528–1545 cm⁻¹, corresponding to the S=C-N fragment, whereas the spectrum of $3 \cdot \text{Et}_2\text{NH}$ contains a band at 1504 cm⁻¹, which is the evidence of the conjugated SCN fragment.⁷ In addition, there is a broad intense band arising from the POC group at 955–978 cm⁻¹. Besides, the IR spectra of 1, 2, 4,

5, **7**, **9** and **10** contain two characteristic bands for the RNH and PNH groups at $3051-3382 \text{ cm}^{-1}$, whereas there is one broad band in the spectra of **6** and **8** at $3151-3167 \text{ cm}^{-1}$, that might be caused by the overlapping of two bands due to the influence of hydrogen bonds. It is noteworthy, that there are no bands for the PNH group in the IR spectrum of $3 \cdot \text{Et}_2\text{NH}$ which is obviously due to the presence of the deprotonated form of **3**. The IR spectrum of the thiourea **6** also contains an intense band at 1707 cm⁻¹, corresponding to the C=O group.

The ${}^{31}P{}^{1}H$ NMR signal of 1, 2, 4–6 and 8–10 in CDCl₃ appears as a singlet at 52.6-53.9 ppm. The signals are in the area characteristic for the neutral NTTU (X = Y = S).^{5a} The ³¹P ${}^{1}H$ NMR spectra of **3**·Et₂NH and **7** contain a singlet signal at 57.5–58.5 ppm. These signals are considerably low-field shifted, confirming the deprotonated form of the phosphorus containing compounds.^{5a} The ¹H NMR spectra of **1–10** in CDCl₃ reveal a single set of signals for the *i*PrO protons: a doublet or two doublets for the CH₃ protons at 1.24–1.42 ppm and a doublet of septets for the CHO protons in the area 4.71-5.00 ppm. The spectrum of 1 contains signals for the *i*PrN group: a doublet for the CH₃ protons at 1.26 ppm and a doublet of septets for the CHN protons at 4.47 ppm. The signals for the Et groups in 2 and in the thiourea fragment of 3.Et₂NH were found as a triplet for the CH₃ protons at 1.15–1.23 ppm and as a doublet of quartets or a broad singlet for the the CH₂ protons at about 3.62 ppm. Furthermore, the spectrum of 3.Et₂NH contains a number of signals for the Et groups of the $Et_2NH_2^+$ cation: a triplet for the CH₃ protons at 1.23 ppm and a quartet for the CH₂ protons at 2.88 ppm. The signals for the Me protons in the spectra of 4-6 are shown as singlets at 2.28-2.34, 2.96 and 3.92 ppm, respectively. The CH₂ protons in the spectra of 8 and 9 were found as a doublet at 4.85-4.91 ppm. The aryl and pyridyl protons in the spectra of 4-10 are shown as a number of signals at 6.71–8.93 ppm. Besides, the spectra of the thioureas 1, 2, 4-6 and 8-10 contain the signals for the PNH proton at 6.62-7.22 ppm. The same signal in the spectrum of 7 is considerably low-field shifted and shown at $\delta = 13.31$ ppm, indicating a strong intramolecular hydrogen bonding between the nitrogen atom of the pyridine function and the hydrogen atom of the phosphorylamide fragment. The signals for the RNH proton are observed at 7.64-11.03 ppm. It is noteworthy that the signals for the alkylNH proton of 1 and 2 are considerably high-field shifted compared to the aryINH or PyNH proton of 4-10. Moreover, the signal for the aryINH proton of 6 is extremely low-field shifted due to a strong intramolecular hydrogen bonding between the oxygen atom of the carbonyl function and the hydrogen atom of the arylNH fragment. The signal for the NH₂ protons of the $Et_2NH_2^+$ cation in the spectrum of $3 \cdot Et_2NH$ is observed as a broad singlet at $\delta = 8.91$ ppm.

Thus, according to NMR spectroscopy data, the thiourea $3 \cdot Et_2 NH$ is deprotonated due to the presence of the $Et_2 NH$ amine, while the thiourea 7 is completely in a zwitterionic form in CDCl₃ (Chart 2). A similar zwitterion formation was observed in the NMR spectra of *N*-(thio)phosphorylated thiosemicarbazides NH₂N(Me)C(S)NHP(X)(O*i*Pr)₂ (X = O, S) and thiourea 2-PyNHC(S)NHP(O)(O*i*Pr)₂.⁸

Crystals of 1 and 4-8 were obtained by slow evaporation of the solvent from a CH_2Cl_2 -n-hexane solution. The molecular structures are shown in Fig. 1–6, whereas the crystal and





Fig. 1 View on the hydrogen bonded dimer of **1**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding were omitted for clarity.



Fig. 2 View on the hydrogen bonded dimer of **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding were omitted for clarity.



Fig. 3 View on the hydrogen bonded dimer of one of the independent molecule of 5. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding were omitted for clarity.



Fig. 4 View on the hydrogen bonded dimer of **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding were omitted for clarity.



Fig. 5 View on the hydrogen bonded dimer of **7**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding were omitted for clarity.



Fig. 6 View on the hydrogen bonded dimer of **8**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms not involved in H-bonding were omitted for clarity.

structure refinement data are given in the Experimental section. The thiourea **5** contains two independent molecules in the unit cell.

Compounds 1 and 4–8 crystallize in the space groups P1, $P2_1/c$, $P2_1/n$ or Pbca. The parameters of the C=S, C-N, P-N and P=S bonds are in the typical range for *N*-thiophosphorylated thiourea derivatives (Table 1).^{5a} The S=C-N-P backbone in 1, 4–6 and 8 has an *E* conformation (Fig. 1–4 and 6), while the same fragment has a *Z* conformation in the structure of 7 (Fig. 5). The crystal structures of 1 (Fig. 1) and 4 (Fig. 2) are stabilized by bifurcated intramolecular hydrogen bonds of the type RN-H···O-P, which are formed between the hydrogen atom

Table 1 Selected bond lengths (Å), and bond angles (°) for 1 and 4-8

			5				8	
	1	4	Molecule A	Molecule B	6	7		
C=S	1.6757(8)	1.662(4)	1.675(4)	1.673(4)	1.6700(14)	$\begin{array}{c} 1.6734(19)\\ 1.9076(8)\\ 1.6729(17)\\ 1.344(2)\\ 1.356(2)\\ 120.14(15)\\ 123.36(14)\\ 116.50(17)\end{array}$	1.6831(19)	
P=S	1.9122(3)	1.9039(12)	1.9162(15)	1.9178(16)	1.9076(5)		1.9194(7)	
P-N	1.6685(7)	1.664(3)	1.675(3)	1.672(3)	1.6750(12)		1.6717(16)	
C-N(P)	1.3792(11)	1.369(4)	1.370(5)	1.372(5)	1.3717(17)		1.393(2)	
C-N(C)	1.3298(11)	1.336(4)	1.335(5)	1.331(5)	1.3492(17)		1.326(2)	
S=C-N(C)	123.30(7)	122.3(3)	122.8(3)	123.6(3)	125.90(11)		123.43(15)	
S=C-N(P)	119.74(6)	121.7(3)	120.7(3)	120.2(3)	119.29(10)		119.30(14)	
N-C(S)-N	116.95(8)	116.0(3)	116.5(3)	116.2(3)	114.77(12)		117.27(16)	
N–P=S	111.48(3)	111.71(11)	116.45(14)	116.54(14)	111.38(4)	116.88(7)	111.49(6)	
C=N–P	129.44(6)	130.2(2)	128.7(3)	127.3(3)	130.05(10)	127.25(14)	129.79(13)	

Table 2 Selected hydrogen bond lengths (Å) and angles (°) for 1 and 4-8

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	170.5(13) 132.0(14) 126.2(14) 164(3) 127(3)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	132.0(14) 126.2(14) 164(3) 127(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	126.2(14) 164(3) 127(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	164(3) 127(3)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	127(3)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	120(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	137(4)
N(2)-H(2)···S(1) 0.903(10) 2.58(2) 3.361(4) N(1A)-H(1A)···S(2A)#1 0.907(10) 2.467(14) 3.362(3) N(2A)-H(2A)···S(1A) 0.905(10) 2.53(3) 3.322(4) M(1)-H(1)···S(2)#1 0.848(18) 2.599(19) 3.4351(12) N(2)-H(2)···O(1) 0.870(18) 2.811(17) 3.0689(16) N(2)-H(2)···O(2) 0.870(19) 2.253(19) 2.9557(15) N(2)-H(2)···O(3) 0.870(19) 1.999(19) 2.6674(17)	179(5)
	145(3)
	169(4)
	146(4)
N(2)-H(2)···O(1) 0.870(18) 2.811(17) 3.0689(16) N(2)-H(2)···O(2) 0.870(19) 2.253(19) 2.9557(15) N(2)-H(2)···O(3) 0.870(19) 1.999(19) 2.6674(17)	169,1(16)
N(2)-H(2)···O(2) 0.870(19) 2.253(19) 2.9557(15) N(2)-H(2)···O(3) 0.870(19) 1.999(19) 2.6674(17)	99
$N(2)-H(2)\cdots O(3)$ $0.870(19)$ $1.999(19)$ $2.6674(17)$	137.8(16)
	132 8(16)
7^e N(2)-H(2)S(2)#1 0.79(2) 2.61(2) 3.3714(18)	163(2)
N(1) + (1) + N(2) $0.80(2)$ $1.94(2)$ $2.615(2)$	143(2)
8^{f} N(1)-H(1)-N(2)#1 0.88 2.60 3.4417(17)	162
N(2) + (1)	126
N(2) - N(2) - O(2) 0.88 2.48 3.074(2)	125
N(2) - H(2) - N(3) 0.88 2.28 2.677(2)	107

^{*a*} Symmetry transformations used to generate equivalent atoms: #1 - x + 2, -y + 2, -z + 2. ^{*b*} Symmetry transformations used to generate equivalent atoms: #1 - x + 2, -y + 1, -z + 2. ^{*c*} Symmetry transformations used to generate equivalent atoms: #1 - x + 2, -y + 1, -z + 1, -y, -z; #2 - x, -y + 1, -z. ^{*d*} Symmetry transformations used to generate equivalent atoms: #1 - x + 1, -y, -z; #2 - x, -y + 1, -z. ^{*d*} Symmetry transformations used to generate equivalent atoms: #1 - x - y + 1, -z, ^{*e*} Symmetry transformations used to generate equivalent atoms: #1 - x - y + 1, -z + 1. ^{*f*} Symmetry transformations used to generate equivalent atoms: #1 - x, -y - z + 1.

of the RNH fragment and two oxygen atoms of the $P(OiPr)_2$ group (Table 2). The crystal structures of 5 (Fig. 3) and 7 (Fig. 5) contain a linear intramolecular hydrogen bond of the type $RN-H\cdots S=P$ (5) or $PN-H\cdots N(pyridine)$ (7), respectively (Table 2). In the former structure the H-bond is formed between the hydrogen atom of the RNH fragment and the sulfur atom of the P=S group, while in the latter structure the H-bond is formed between the hydrogen atom of the phosphorylamide group and the nitrogen atom of the pyridine ring. It is worthy to note, that the distance $H(1)\cdots N(3)$ in the structure of 7 is considerably shortened (Table 2), indicating a strong intramolecular hydrogen bonding formation. The crystal structures of 6 (Fig. 4) and 8 (Fig. 6) are stabillized by trifurcated intramolecular hydrogen bonds (Table 2). Two of the three H-bonds are of the type RN-H···O-P, similar to those observed for 1 and 4, while the third H-bond is formed between the same hydrogen atom of the RNH group and the carbonyl oxygen atom in 6 or the nitrogen atom of the pyridine ring in **8**. Furthermore, the crystal structures of the thioureas **1**, **4–6** and **8** are additionally stabilized by intermolecular hydrogen bonds of the type PN–H····S^{#1}==C^{#1} (Fig. 1–4 and 6, Table 2), which are formed between the S atoms of the C=S groups and the H atoms of the PNH fragment of two molecules. The similar intermolecular hydrogen bonds were observed in the structure of **7**. However, these bonds are formed between the S atoms of the C=S groups and the C=S groups and the H atoms of the RNH fragment of two molecules (Fig. 5, Table 2). As a result of intermolecular interactions, centrosymmetric dimers are formed in the crystal structures of **1** and **4–8**. Additionally, the centrosymmetric dimers of **5–8** form π ··· π stacking interactions between the aryl (**5** and **6**) or pyridine (**7** and **8**) rings (Fig. 7–10, Table 3). These interactions produce polymeric chains in the crystal structures.

Recently, we have studied the competitive transport properties of 1 and 7.^{5c,d} In this work we present the transport properties of



Fig. 7 View on the $\pi \cdots \pi$ stacking interactions between the hydrogen bonded dimers of 5. Hydrogen atoms except NH were omitted for clarity.



Fig. 8 View on the $\pi \cdots \pi$ stacking interactions between the hydrogen bonded dimers of 6. Hydrogen atoms except NH were omitted for clarity.



Fig. 9 View on the $\pi \cdots \pi$ stacking interactions between the hydrogen bonded dimers of 7. Hydrogen atoms except NH were omitted for clarity.

2–6 and **8–10**. The ligands shown in Chart 1 can be divided into three groups. The first group displays thiophosphorylated thioureas **1–3**, containing the alkyl substituents at the thiocarbonyl group. In the second group the compounds **4–6**, containing the substituted benzene rings, have been combined. The third group comprises of thioureas **7–10** with nitrogen-containing heterocycles at the thiocarbonyl group. This division is very useful to discuss the results of the membrane transport investigations summarized in Table 4, since the number and type of the substituent at the thiocarbonyl group of an ionophore strongly determines its binding efficiency and selectivity.^{5c,d}

Recently, it was established that using the thiourea **1** as an ionophore leads to no cations in the receiving phase.^{5*c*,*d*} However, this ligand shows moderate extraction properties of Ag^{I} from a water phase into an organic phase during the transport experiment. Cu^{II} cations are also extracted into the organic phase, but in a 1.77 times smaller amount. The thiourea **2**, containing the EtNH group instead of the *i*PrNH fragment in **1**, shows similar extraction properties as **1**. However, it extracts both Ag^{I} and Cu^{II} in the membrane phase more efficiently (by 9)



Fig. 10 View on the $\pi \cdots \pi$ stacking interactions between the hydrogen bonded dimers of 8. Hydrogen atoms except NH were omitted for clarity.

Table 3 Selected $\pi \cdots \pi$ interactions for 5–8

	Cg(I)	Cg(J)	Cg–Cg (Å)	Dihedral angle (°)	β (°)
5 ^{<i>a</i>}	Cg(1)	$Cg(1)^{\#1}$	4.087(2)	0	25.06
	Cg(2)	$Cg(2)^{\#2}$	4.140(3)	0	24.37
6 ^b	Cg(1)	$Cg(1)^{\#1}$	3.7095(12)	0	18.25
7^c	Cg(1)	$Cg(1)^{\#1}$	3.8611(12)	2	31.06
	Cg(1)	$Cg(1)^{\#2}$	3.8612(12)	2	28.91
8^d	Cg(1)	$Cg(1)^{\#1}$	3.9362(13)	0	26.47
	Cg(1)	$Cg(1)^{\#2}$	3.9850(13)	0	26.79

^a Symmetry codes: #1 -x + 1, -y + 1, -z + 1; #2 -x + 2, -y, -z + 1. Cg(1): C(8)–C(9)–C(10)–C(11)–C(12)–C(13), Cg(2): C(8A)–C(9A)–C(10A)–C(11A)–C(12A)–C(13A). ^b Symmetry codes: #1 -x + 1, -y + 1, -z + 1. Cg(1): C(8)–C(9)–C(10)–C(11)–C(12)–C(13). ^c Symmetry codes: #1 -x + 1/2, y - 1/2, z; #2 -x + 1/2, y + 1/2, z. Cg(1): N(3)–C(8)–C(9)–C(10)–C(11)–C(12). ^d Symmetry codes: #1 -x, -y, -z; #2 -x + 1, -y, -z. Cg(1): N(3)–C(9)–C(10)–C(11)–C(12)–C(13).

and 13%, respectively). This is, obviously, due to the presence of the less sterically demanding ethyl group. The thiourea 3 also shows no transport properties. Furthermore, only a very small amount of the Ag^I (3%) and Cu^{II} (1.6%) ions were found in the membrane phase, which became pale yellow and muddy during the first few hours of the experiment. It was established that compound 3 decomposes rather rapidly under the experimental conditions. It is well known, that NTTUs, containing strong σ donor substituents at the thiocarbonyl group, are significantly decomposed in solution.^{5a} In general, the extraction properties of the thioureas $RNHC(S)NHP(S)(OiPr)_2$ (R = H, Et, *iPr*, *tBu*) towards Ag^I and Cu^{II} from the source phase to the membrane phase decrease with increasing of the bulkiness of the substituent.^{5c,d} Moreover, the compound $H_2NC(S)NHP(S)(OiPr)_2$ transports both AgI and CuII to a receiving phase in approximately equal amounts, and does not show transport selectivity of the two cations. It is necessary to note, that the degree of transport of both cations is rather low and is of the order of 2%. 5c,d

Compounds **4–6** contain the substituted benzene functions at the C=S fragment. The thioureas **4** and **5** show no transport properties and extract both Ag^I and Cu^{II} ions with the values of 32–37 and 29–40%, respectively (Table 4). In general, the transport and extraction properties of **4** and **5** are very similar to those of the previously described thioureas RNHC(S)NHP(S)(O*i*Pr)₂ (R = Ph, α -naphthyl).^{5*c*,d} Contrariwise, the thiourea **6** displays the best transport properties for Ag^I for all the ligands studied (Table 4). Furthermore, it also transports Cu^{II} but in a 15.5 times smaller amount. However, a very high amount of Cu^{II} was found in the membrane phase (92%). The sums ^{Ag}T_r% + ^{Ag}T_M% and ^{Cu}T_r% + ^{Cu}T_M% are 98% and 94%, respectively. Thus,

Table 4 The average flux rate (*J*) values for the competitive metal ion transport studies involving 1–10. The experimental conditions were as follows: pH of the source phase = 5.5, pH of receiving phase = 1.0 and concentration of ligand = $0.002 \text{ mol dm}^{-3}$

	Metal ion transport, $J/(\text{mol } 24 \text{ h}) \times 10^6$									
Ligand number	1^{a}	2	3	4	5	6	7^a	8	9	10
Co^{II} , Ni^{II} , Zn^{II} , Cd^{II} , Pb^{II}										
Cu ^{II}						2			6	59
Ag ^I		_				31			4	8
$^{Ag}T_{r}\%^{b}$	_					31			4	8
$^{\text{Ag}}T_{\text{M}}\%^{c}$	69	78	3	32	37	67	85	78	72	84
$C^{u}T_{r}^{m}/6^{b}$	_					2			6	59
$^{Cu}T_{M}\%^{c}$	39	52	1.6	29	40	92	70	64	67	38
$Ag T_r \% + Ag T_M \%$	69	78	3	32	37	98	85	78	76	92
$C^{u}T_{r}^{0}$ + $C^{u}T_{M}^{0}$	39	52	1.6	29	40	94	70	64	73	97
$\eta_r (Ag^I/Cu^{II})^{d^{11}}$	_					15.5			0.67	0.14
$\eta_{\rm M}({\rm \tilde{Ag}^{\rm I}}/{\rm Cu^{\rm II}})^e$	1.77	1.50	1.88	1.10	0.93	0.73	1.21	1.22	1.07	2.21
	1., ,	1.50	1.00		0.95			1.22 Cu	1.07	

^{*a*} The data from [5c,d]. ^{*b*} Ag T_r % and ^{Cu} T_r % = percentage of Ag^I and Cu^{II} transported into the receiving phase. ^{*c*} Ag T_M % and ^{Cu} T_M % = percentage of Ag^I and Cu^{II} transported into the membrane phase. ^{*d*} η_r (Ag^I/Cu^{II}) = ^{Ag} T_r %. ^{*e*} η_M (Ag^I/Cu^{II}) = ^{Ag} T_M %.

compound **6** almost completely retrieves both Ag^{I} and Cu^{II} from the source phase. These transport and extraction properties of the ligand **6** are, obviously, explained by the presence of two coordination functions: C(S)NHP(S) and MeO(O)C.

The compounds 7–10 are grouped together because these thiophosphorylated thioureas are ligands that have nitrogen-containing heterocycles at the thiocarbonyl group. The compounds 7 and 8 show no transport properties and extract Ag^I and Cu^{II} similarly (Table 4). However, incorporation of the methylene fragment between the pyridyl and thiocarbonyl groups leads to a slightly decrease of the extraction of Ag^I and Cu^{II}. This is due to the lability (a relatively easier rotation along the HN-C(S) bond) of the 2-PyCH₂NH fragment compared to 2-PyNH. The thiourea 9 extracts both the Ag^I and Cu^{II} cations at the same degree as 7 and 8 but also shows some transport properties towards the same cations (Table 4). This might be explained by the formation of less stable coordination compounds of 9 and Ag^I and/or Cu^{II} due to the 3-Py fragment instead of 2-Py. The thiourea 10 displays the best transport properties for Cu^{II} for all the ligands investigated (Table 4). It also transports Ag^I but in a about 7.4 times smaller amount. This is due to the presence of the triazole ring, which shows a great affinity towards Cu^{II},⁹ in the structure of 10. Furthermore, a high amount of Ag^I was found in the membrane phase (84%). The sums ${}^{Ag}T_{r}\% + {}^{Ag}T_{M}\%$ and ${}^{Cu}T_{r}\% + {}^{Cu}T_{M}\%$ are 92% and 97%, respectively. Thus, compound 10 almost completely retrieves both Ag^I and Cu^{II} from the source phase similar to the thiourea 6.

Throughout the transport experiments, we have incorporated 4 $\times 10^{-3}$ mol dm⁻³ palmitic acid in the membrane phase. It was established, that at this concentration and under the experimental conditions employed, no metal ion transport was observed when only palmitic acid was present in the membrane phase. Palmitic acid is widely used in transport experiments involving a variety of ligands as ionophores.^{5c,d,10,11} A major role of palmitic acid is to aid the transpost process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase, giving rise to charge neutralisation of the metal cation being transported through ion pairing or adduct formation. In this manner the uptake of lipophobic nitrate anions into the organic phase is avoided. An additional benefit of adding lipophilicity in

the form of the long-chain acid is to inhibit any bleeding of partially hydrophilic species (such as the protonated or deprotonated ionophore and/or its corresponding charged metal complex) from the organic membrane phase into either of the aqueous phases.^{11–13} It was observed, that the thioureas **1**, **2** and **4–10** alone are not effective carriers for the studied metal cations. Even the ${}^{M}T_{M}\%$ values are less than 0.5% for about 3 days during the separate experiments for each metal cations. Furthermore, no cations were observed in the receiving phase. This is obviously due to the considerable solubilities of the complexed forms of neutral **1**, **2** and **4–10** in the aqueous source phase. Thus, the thioureas **1**, **2** and **4–10** and palmitic acid show the cooperative action of the two components as a carrier.

On the other hand, the obtained transport properties of the thioureas **1–10** might be also explained by the differences in the complexes formed with the studied metal cations. For the Co^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Pb^{II} cations the formation of complexes of the [ML₂] composition was exclusively observed.^{5,8} Furthermore, the dithio-containing **NTTU** (X, Y = S) ligands are coordinated towards the same metal cations through the sulfur atoms of the C=S and P=S groups. However, it was established, that the **NTTU** compounds, containing the pyridine function at the thiocarbonyl group, are additionally coordinated through the pyridine nitrogen atom.^{8b} Contrariwise, the Ag^I and Cu^{II} cations form polynuclear complexes with the **NTTU** (X, Y = S) ligands of the 1 : 1 metal to ligand ratio (Chart 3).^{5c,d,14} Moreover, the



formation of such polymeric compounds might lead to the formation of the cyclic crown ether-like structures of a different size (Chart 3). Cavities of these cycles might be also suitable for the coordination of additional metals through the sulfur atoms of the thiocarbonyl groups. Furthermore, the donor oxygen and sulfur atoms of the S==P(O*i*Pr)₂ fragments together with donor functions of the substituent at the thiocarbonyl group might also possesses coordination properties towards metals.^{14*d*}

As can be seen for Table 4, the sum ${}^{Ag}T_{M}\% + {}^{Cu}T_{M}\%$ for 1, 2 and 6-10 exceeds 100%. This indicates that these thioureas must be simultaneously coordinating to both AgI and CuII ions which gives strong evidence for the formation of oligomeric heteronuclear species in the membrane phase. This explains that no Co^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Pb^{II} cations were extracted even into the organic phase during the transport conditions. However, moderate amounts of the Ni^{II} cations were observed in the membrane phase when the thioureas 4 ($^{Ni}T_M$ % 3.8) and 5 ($^{Ni}T_M$ % 4.6) were used as ionophores. This might be explained by the fact that the sum ${}^{Ag}T_{M}\%$ + ${}^{Cu}T_{M}\%$ for 4 and 5 is 61 and 77%, respectively, and hence not all amount of these thioureas is coordinated towards Ag^{I} and Cu^{II} . Furthermore, the affinity of 4 and 5 to extract Ni^{II} cations among the rest metals might be explained by the formation of a 1,3-N,S-coordinated complex form in $CHCl_{3}$, ^{5e} which might be more suitable for extraction upon the experimental conditions used for transport experiments. For the Co^{II}, Zn^{II}, Cd^{II} and Pb^{II} cations the formation of complexes with an exclusive 1,5-S,S'-coordination mode of ligands was observed.5,8 Furthermore, the differences for the obtained transport and extraction properties of 1, 2 and 4-10 towards the studied metal cations might be explained by significantly different stability constants of the formed complexes as well as the used experimental time (24 h) is not enough for the transport of the Co^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Pb^{II} cations. However, increasing of the experimental time leads to the decomposition of 1, 2 and 4-10 in solution as it was observed for the thiourea 3 (see above).

Conclusions

In summary, we have synthesized a wide range of N-thiophosphorylated thioureas 1-10 by the addition of thiophosphorylisothiocyanate to the corresponding amine.

According to IR and NMR spectroscopy data, $3 \cdot \text{Et}_2 \text{NH}$ is deprotonated due to the presence of the Et₂NH amine, while the thiourea 7 is completely in a zwitterionic form.

Single crystal X-ray diffraction studies showed that an *E* arrangement of the C=S and P–N bonds in the S=C–N–P backbones was found for the thioureas 1, 4–6 and 8. The thiourea 7 was observed as a *Z* conformational isomer. In the crystal, the thioureas 1 and 4–8 form linear, bi- or trifurcated hydrogen bonds. Furthermore, their crystal structures are stabilized by two intermolecular hydrogen bonds, which in turn lead to a centrosymmetric dimer formation. Additionally, the hydrogen bonded dimers of 5–8 are packed to polymeric chains through the $\pi \cdots \pi$ stacking interactions between aryl or pyridyl rings.

The thioureas 1-10 have been investigated for their transport properties towards the Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Ag^I, Cd^{II} and Pb^{II} cations. It was established, that the ligands 6 and 10 are the most efficient for the transport of Ag^I and Cu^{II}, respectively. Furthermore, the same two ligands almost completely retrieve both Ag^I and Cu^{II} from the source phase.

Experimental

General procedures

Infrared spectra (Nujol) were recorded with a Thermo Nicolet 380 FT-IR spectrometer in the range 400–3600 cm⁻¹. NMR spectra in CDCl₃ were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ¹H and ³¹P{¹H} NMR spectra were recorded at 299.948, and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and 85% H₃PO₄ (³¹P{¹H}). Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

Synthesis of 1–10

A solution of isopropylamine, ethylamine, diethylamine, 2,5dimethylaniline, 4-(dimethylamino)aniline, methyl 2-aminobenzoate, 2-aminopyridine, 2-(aminomethyl)pyridine, 3-(aminomethyl)pyridine or 4-amino-4H-1,2,4-triazole (5 mmol; 0.296, 0.225, 0.366, 0.606, 0.681, 0.756, 0.471, 0.541, 0.541 or 0.420 g) in anhydrous CH₂Cl₂ (15 mL) was treated under vigorous stirring with a solution of (*i*PrO)₂P(S)NCS (6 mmol, 1.436 g) in the same solvent (15 mL). The mixture was stirred for 1 h. The solvent was removed in a vacuum, and the product was purified by recrystallisation from a 1 : 5 (v/v) mixture of CH₂Cl₂ and n-hexane.

1. Yield: 1.402 g (94%). IR v (cm⁻¹): 640 (P=S), 964 (POC), 1543 (S=C-N), 3090, 3382 (NH). ¹H NMR: δ = 1.26 (d, ${}^{3}J_{\rm H,\rm H}$ = 6.6 Hz, 6H, CH₃, *i*PrN), 1.33 (d, ${}^{3}J_{\rm H,\rm H}$ = 6.2 Hz, 6H, CH₃, *i*PrO), 1.35 (d, ${}^{3}J_{\rm H,\rm H}$ = 6.2 Hz, 6H, CH₃, *i*PrO), 1.35 (d, ${}^{3}J_{\rm H,\rm H}$ = 6.2 Hz, 6H, CH₃, *i*PrO), 4.47 (d. sept, ${}^{3}J_{\rm HNCH}$ = 8.0 Hz, ${}^{3}J_{\rm H,\rm H}$ = 6.5 Hz, 1H, NCH), 4.79 (d. sept, ${}^{3}J_{\rm POCH}$ = 10.6 Hz, ${}^{3}J_{\rm H,\rm H}$ = 6.2 Hz, 2H, OCH), 6.86 (br. s, 1H, PNH), 7.64 (br. s, 1H, alkylNH) ppm. ${}^{31}P\{^{1}H\}$ NMR: δ = 52.8 ppm. Calc. for C₁₀H₂₃N₂O₂PS₂ (298.40): C, 40.25; H, 7.77; N, 9.39. Found: C, 40.28; H, 7.74; N, 9.44%.

2. Yield: 1.137 g (80%). IR ν (cm⁻¹): 639 (P=S), 957 (POC), 1545 (S=C-N), 3103, 3374 (NH). ¹H NMR: δ = 1.23 (t, ³*J*_{H,H} = 7.3 Hz, 3H, CH₃, Et), 1.31 (d, ³*J*_{H,H} = 6.0 Hz, 6H, CH₃, *i*Pr), 1.33 (d, ³*J*_{H,H} = 6.0 Hz, 6H, CH₃, *i*Pr), 3.63 (d, q, ³*J*_{HCNH} = 9.0 Hz, ³*J*_{H,H} = 7.2 Hz, 2H, CH₂), 4.77 (d. sept, ³*J*_{POCH} = 10.6 Hz, ³*J*_{H,H} = 6.1 Hz, 2H, OCH), 6.62 (br. s, 1H, PNH), 7.83 (br. s, 1H, alkylNH) ppm. ³¹P{¹H} MR: δ = 52.7 ppm. Calc. for C₉H₂₁N₂O₂PS₂ (284.37): C, 38.01; H, 7.44; N, 9.85. Found: C, 38.07; H, 7.39; N, 9.89%.

3·Et₂NH. Yield: 0.733 g (76%). IR v (cm⁻¹): 617 (P=S), 970 (POC), 1504 (SCN). ¹H NMR: $\delta = 1.15$ (t, ³ $J_{H,H} = 7.1$ Hz, 6H, CH₃, Et), 1.23 (t, ³ $J_{H,H} = 7.3$ Hz, 6H, CH₃, Et₂NH₂⁺), 1.29 (d, ³ $J_{H,H} = 6.2$ Hz, 12H, CH₃, *i*Pr), 2.88 (q, ³ $J_{H,H} = 7.3$ Hz, 4H, CH₂, Et₂NH₂⁺), 3.62 (br. s, 4H, CH₂), 4.79 (d. sept, ³ $J_{POCH} = 10.6$ Hz, ³ $J_{H,H} = 6.2$ Hz, 2H, oCH), 8.91 (br. s, 2H, NH₂, Et₂NH₂⁺) ppm. ³¹P{¹H} NMR: $\delta = 58.5$ ppm. Calc. for C₁₅H₃₆N₃O₂PS₂ (385.56): C, 46.73; H, 9.41; N, 10.90. Found: C, 46.68; H, 9.49; N, 10.81%.

4. Yield: 1.658 g (92%). IR v (cm⁻¹): 638 (P=S), 955 (POC), 1525 (S=C-N), 3084, 3365 (NH). ¹H NMR: $\delta = 1.39$ (d, ³ $J_{H,H} = 6.2$ Hz, 6H, CH₃, *i*Pr), 1.41 (d, ³ $J_{H,H} = 6.2$ Hz, 6H, CH₃, *i*Pr), 2.28 (s, 3H, CH₃, Me), 2.34 (s, 3H, CH₃, Me), 4.89 (d. sept, ³ $J_{POCH} = 10.5$ Hz, ³ $J_{H,H} = 6.2$ Hz, 2H, OCH, *i*Pr), 7.05 (d. d, ³ $J_{H,H} = 7.9$ Hz, ⁴ $J_{H,H} = 1.2$ Hz, 1H, *p*-H, C₆H₃), 7.10 (br. s, 1H, PNH), 7.16 (d, ³ $J_{H,H} = 7.8$ Hz, 1H, *m*-H, C₆H₃), 7.22 (br. s, 1H, *o*-H, C₆H₃), 9.30 (s, 1H, aryINH) ppm. ³¹P{¹H} NMR: $\delta = 52.7$ ppm. Calc. for C₁₅H₂₅N₂O₂PS₂ (360.47): C, 49.98; H, 6.99; N, 7.77. Found: C, 49.92; H, 7.04; N, 7.71%.

5. Yield: 1.6718 g (89%). IR v (cm⁻¹): 632 (P=S), 974 (POC), 1529 (S=C-N), 3051, 3215 (NH). ¹H NMR: $\delta = 1.39$ (d, ${}^{3}J_{H,H} = 6.1$ Hz, 6H, CH₃, *i*Pr), 1.40 (d, ${}^{3}J_{H,H} = 6.1$ Hz, 6H, CH₃, *i*Pr), 2.96 (s, 6H, CH₃, Me), 4.87 (d. sept, ${}^{3}J_{POCH} = 10.6$ Hz, ${}^{3}J_{H,H} = 6.1$ Hz, 2H, OCH, *i*Pr), 6.71 (d, ${}^{3}J_{H,H} = 8.7$ Hz, 2H, *o*-H, C₆H₄), 6.98 (d, ${}^{3}J_{PNH} = 9.1$ Hz, 1H, PNH), 7.29 (d, ${}^{3}J_{H,H} = 8.6$ Hz, 2H, *m*-H, C₆H₄), 9.34 (s, 1H, arylNH) ppm. ${}^{31}P\{{}^{1}H\}$ NMR: $\delta = 52.6$ ppm. Calc. for C₁₅H₂₆N₃O₂PS₂ (375.48): C, 47.98; H, 6.98; N, 11.19. Found: C, 48.05; H, 7.07; N, 11.13%.

6. Yield: 1.874 g (96%). IR *v* (cm⁻¹): 647 (P=S), 964 (POC), 1528 (S=C-N), 1707 (C=O), 3151 (NH). ¹H NMR: *δ* = 1.39 (d, ³J_{H,H} = 6.2 Hz, 6H, CH₃, *i*Pr), 1.41 (d, ³J_{H,H} = 6.2 Hz, 6H, CH₃, *i*Pr), 1.41 (d, ³J_{H,H} = 6.2 Hz, 6H, CH₃, *i*Pr), 3.92 (s, 3H, CH₃, Me), 4.91 (d. sept, ³J_{POCH} = 10.6 Hz, ³J_{H,H} = 6.2 Hz, 2H, OCH, *i*Pr), 7.23 (d. t, ³J_{H,H} = 7.8 Hz, ⁴J_{H,H} = 1.5 Hz, 1H, *m*-H, C₆H₄), 7.54 (d. t, ³J_{H,H} = 7.9 Hz, ⁴J_{H,H} = 1.6 Hz, 1H, *p*-H, C₆H₄), 7.18 (br. s, 1H, PNH), 7.98 (d. d, ³J_{H,H} = 7.9 Hz, ⁴J_{H,H} = 1.6 Hz, 1H, *m*-H, C₆H₄), 11.03 (s, 1H, arylNH) ppm. ³¹P {¹H</sup>} NMR: *δ* = 53.9 ppm. Calc. for C₁₅H₂₃N₂O₄PS₂ (390.45): C, 46.14; H, 5.94; N, 7.17. Found: C, 46.08; H, 5.98; N, 7.12%.

7. Yield: 1.517 g (91%). IR v (cm⁻¹): 639 (P=S), 962 (POC), 1530 (S=C-N), 3182, 3216 (NH). ¹H NMR: δ = 1.41 (d, ³*J*_{H,H} = 6.2 Hz, 6H, CH₃, *i*Pr), 1.42 (d, ³*J*_{H,H} = 6.2 Hz, 6H, CH₃, *i*Pr), 5.00 (d. sept, ³*J*_{POCH} = 10.6 Hz, ³*J*_{H,H} = 6.2 Hz, 2H, OCH, *i*Pr), 6.87–7.08, 7.61–7.76, 8.13–8.24 (m, 4H, Py), 9.39 (s, 1H, PyNH), 13.31 (br. s, 1H, PNH) ppm. ³¹P{¹H} NMR: δ = 57.5 ppm. Calc. for C₁₂H₂₀N₃O₂PS₂ (333.40): C, 43.23; H, 6.05; N, 12.60. Found: C, 43.29; H, 6.11; N, 12.53%.

8. Yield: 1.511 g (87%). IR v (cm⁻¹): 643 (P=S), 969 (POC), 1534 (S=C-N), 3167 (NH). ¹H NMR: $\delta = 1.31$ (d, ³*J*_H, H = 6.1 Hz, 6H, CH₃, *i*Pr), 1.37 (d, ³*J*_{H,H} = 6.1 Hz, 6H, CH₃, *i*Pr), 4.83 (d. sept, ³*J*_{POCH} = 10.5 Hz, ³*J*_{H,H} = 6.1 Hz, 2H, OCH, *i*Pr), 4.91 (d, ³*J*_{HCNH} = 4.1 Hz, 2H, CH₂), 6.95 (br. s, 1H, PNH), 7.17–7.39, 7.63–7.78, 8.48–8.61 (m, 4H, Py), 8.96 (br. s, 1H, alkylNH) ppm. ³¹P{¹H} NMR: $\delta = 53.8$ ppm. Calc. for C₁₃H₂₂N₃O₂PS₂ (347.43): C, 44.94; H, 6.38; N, 12.09. Found: C, 44.86; H, 6.42; N, 12.14%.

9. Yield: 1.372 g (79%). IR v (cm⁻¹): 646 (P=S), 978 (POC), 1537 (S=C-N), 3179, 3248 (NH). ¹H NMR: δ = 1.26 (d, ³*J*_{H,H} = 6.1 Hz, 6H, CH₃, *i*Pr), 1.27 (d, ³*J*_{H,H} = 6.1 Hz, 6H, CH₃, *i*Pr), 4.75 (d. sept, ³*J*_{POCH} = 10.5 Hz, ³*J*_{H,H} = 6.1 Hz, 2H, OCH, *i*Pr), 4.85 (d, ³*J*_{HCNH} = 4.6 Hz, 2H, CH₂), 7.22 (br. s, 1H, PNH), 7.17–7.37, 7.61–7.81, 8.52–8.65 (m, 4H, Py), 8.31 (br. s, 1H, alkylNH) ppm. ³¹P{¹H} NMR: δ = 52.7 ppm. Calc. for C₁₃H₂₂N₃O₂PS₂ (347.43): C, 44.94; H, 6.38; N, 12.09. Found: C, 45.02; H, 6.33; N, 12.02%.

10. Yield: 1.520 g (94%). IR v (cm⁻¹): 637 (P=S), 977 (POC), 1535 (S=C-N), 3098, 3264 (NH). ¹H NMR: $\delta = 1.24$ (d, ³ $J_{H,H} = 6.2$ Hz, 6H, CH₃, *i*Pr), 1.29 (d, ³ $J_{H,H} = 6.1$ Hz, 6H, CH₃, *i*Pr), 4.71 (d. sept, ³ $J_{POCH} = 10.7$ Hz, ³ $J_{H,H} = 6.1$ Hz, 2H, OCH, *i*Pr), 7.18 (br. s, 1H, PNH), 8.72 (s, 1H, arylNH), 8.93 (s, 2H, CH, triazole) ppm. ³¹P{¹H} NMR: $\delta = 53.1$ ppm. Calc. for C₉H₁₈N₅O₂PS₂ (323.37): C, 33.43; H, 5.61; N, 21.66. Found: C, 33.49; H, 5.56; N, 21.58%.

Membrane transport

An aqueous source phase (10 mL), containing an equimolar mixture of the seven metal ions Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Ag^I, Cd^{II} and Pb^{II} as their nitrate salts dissolved in a pH 5.5 buffer solution (CH₃COOH/NaOOCCH₃), and an aqueous receiving phase (30 mL of 0.1 mol dm⁻³ HNO₃, pH = 1.0) were separated by a water presaturated chloroform membrane phase containing the ligand (50 mL) and 4×10^{-3} mol dm⁻³ palmitic acid. The concentration of the metal ions was 1×10^{-2} mol dm⁻³ and that of the chosen ligand was 2×10^{-3} mol dm⁻³. The mentioned pH values of the source and receiving phases, as well as the ligand concentration in the membrane phase, were found to be the optimum for the use of the NTTU ligands as ionophores.^{5c,d} The slightly modified cell details are the same as those described by Lindoy et al.¹⁵ The membrane phase, the source phase and the receiving phase were then transferred in this respective order into the cells. The cells were thermostated at 25 °C and stirred at 10 rpm. Under these conditions, not only was the stirring process consistent, but also the interfaces between the organic membrane and the two aqueous phases remained flat and well defined and transport allowed to take place, against a back gradient of protons. The cells were covered with cover slips in order to prevent evaporation of solvents over the 24 h period and then entirely covered by aluminium foil in order to prevent the lightinduced reduction of Ag^I in the source phase. All transport experiments were terminated after 24 h and the amount of metal ion transported from the source phase to the receiving phase over this period was determined by atomic absorption spectroscopy (AAS). Small samples for analysis were taken from both the source and receiving phases of each duplicate run after each experiment and analyzed. The average flux rate, J (mol per 24 h), for each transport experiment was calculated based on the quantity of metal ions transported into the receiving phase in a 24 h period. The transport results are quoted as the average values obtained from the duplicate runs carried out in parallel; in all cases the flux values obtained did not differ by more than 5%. J values equal to or less than 2.2×10^{-8} mol per 24 h were assumed to be within experimental error of zero and have been ignored in the analysis of results.

Under the experimental conditions employed, no metal ion transport was observed when only palmitic acid was present in the membrane phase.

X-Ray crystallography

The X-ray data of 1 and 4–7 were collected on a STOE IPDS-II diffractometer with graphite-monochromatised Mo-K α radiation generated by a fine-focus X-ray tube operated at 50 kV and

40 mA. The reflections of the images were indexed, integrated and scaled using the X-Area data reduction package.¹⁶ Data were corrected for absorption using the PLATON program.¹⁷ The Xray data for 8 were collected on a Mar345 image plate detector using Mo-Ka radiation (Zr-filter). The data were integrated with the crysAlisPro software.¹⁸ The structures were solved by direct methods using the SHELXS97 program¹⁹ and refined first isotropically and then anisotropically using SHELXL-97.19 Hydrogen atoms of 1 and 4–7 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. Non-hydrogen atoms of 8 were anisotropically refined and the hydrogen atoms were placed on calculated positions in riding mode with temperature factors fixed at 1.2 times Ueq of the parent atoms and 1.5 times U_{eq} for methyl groups. Figures were generated using the program Mercury.²⁰

Crystal data for 1. $C_{10}H_{23}N_2O_2PS_2$, $M_r = 298.39$ g mol⁻¹, triclinic, space group $P\bar{I}$, a = 8.7411(4), b = 9.4953(4), c = 10.2409(5) Å, $\alpha = 94.511(2)$, $\beta = 99.974(2)$, $\gamma = 94.849(2)^\circ$, V = 830.37(7) Å³, Z = 2, $\rho = 1.193$ g cm⁻³, μ (Mo-K α) = 0.411 mm⁻¹, reflections: 21707 collected, 6020 unique, $R_{int} = 0.0171$, $R_1(all) = 0.0322$, $wR_2(all) = 0.0811$.

Crystal data for 4. $C_{15}H_{25}N_2O_2PS_2$, $M_r = 360.46 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/c$, a = 9.6981(5), b = 16.1422(10), c = 13.1345(6) Å, $\beta = 111.037(3)^\circ$, V = 1919.14(18) Å³, Z = 4, $\rho = 1.248 \text{ g cm}^{-3}$, μ (Mo-K α) = 0.368 mm⁻¹, reflections: 31989 collected, 3640 unique, $R_{\text{int}} = 0.0974$, $R_1(\text{all}) = 0.0937$, $wR_2(\text{all}) = 0.1351$.

Crystal data for 5. $C_{15}H_{26}N_3O_2PS_2$, $M_r = 375.48 \text{ g mol}^{-1}$, triclinic, space group $P\bar{I}$, a = 10.2581(6), b = 13.1606(7), c = 14.9343(8) Å, $\alpha = 90.718(3)$, $\beta = 107.751(3)$, $\gamma = 93.285(2)^\circ$, V = 1916.07(18) Å³, Z = 4, $\rho = 1.302$ g cm⁻³, μ (Mo-K α) = 0.373 mm⁻¹, reflections: 33787 collected, 6750 unique, $R_{int} = 0.0567$, $R_1(all) = 0.0781$, $wR_2(all) = 0.1522$.

Crystal data for 6. $C_{15}H_{23}N_2O_4PS_2$, $M_r = 390.44$ g mol⁻¹, monoclinic, space group $P2_1/n$, a = 7.7008(9), b = 20.249(3), c = 12.5512(17) Å, $\beta = 95.990(6)^\circ$, V = 1946.5(5) Å³, Z = 4, $\rho = 1.332$ g cm⁻³, μ (Mo-K α) = 0.376 mm⁻¹, reflections: 52859 collected, 5030 unique, $R_{int} = 0.0388$, $R_1(all) = 0.0411$, $wR_2(all) = 0.0845$.

Crystal data for 7. $C_{12}H_{20}N_3O_2PS_2$, $M_r = 333.40 \text{ g mol}^{-1}$, orthorhombic, space group *Pbca*, a = 14.3388(7), b = 6.9545(4), c = 33.6884(18) Å, V = 3359.4(3) Å³, Z = 8, $\rho = 1.318 \text{ g cm}^{-3}$, μ (Mo-K α) = 0.416 mm⁻¹, reflections: 68595 collected, 4341 unique, $R_{\text{int}} = 0.0820$, $R_1(\text{all}) = 0.0697$, $wR_2(\text{all}) = 0.1030$.

Crystal data for 8. $C_{13}H_{22}N_3O_2PS_2$, $M_r = 347.43$ g mol⁻¹, monoclinic, space group $P2_1/n$, a = 7.6949(8), b = 17.153(2), c = 13.2985(13) Å, $\beta = 90.175(10)^\circ$, V = 1755.3(3) Å³, Z = 4, $\rho = 1.315$ g cm⁻³, μ (Mo-K α) = 0.401 mm⁻¹, reflections: 8683 collected, 3210 unique, $R_{int} = 0.028$, $R_1(all) = 0.0394$, $wR_2(all) = 0.1073$.

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