Complexes of *N*-thiophosphorylthioureas (HL) with copper(I). Crystal structures of $[Cu_3L_3]$ and $[Cu(PPh_3)_2L]$ chelates†

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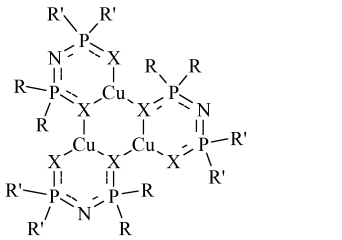
Reaction of the potassium salts of *N*-thiophosphorylated thioureas of common formula $RC(S)NHP(S)(OiPr)_2$ [R = morpholin-*N*-yl (HL^a), piperidin-*N*-yl (HL^b), NH_2 (HL^c), $PhCH_2NH$ (HL^d)] with $Cu(PPh_3)_3I$ in aqueous $EtOH/CH_2Cl_2$ leads to mononuclear $[Cu(PPh_3)_2L–S,S']$ complexes. Using copper(I) iodide instead of $Cu(PPh_3)_3I$, polynuclear complexes $[Cu_n(L–S,S')_n]$ were obtained. The structures of these compounds were investigated by ES-MS, elemental analyses, ^1H and ^{31}P NMR in solution, IR and ^{31}P solid-state MAS NMR spectroscopy. The crystal structures of $[Cu_3L_3{}^a]$ and $[Cu(PPh_3)_2L^b]$ were determined by single-crystal X-ray diffraction.

Introduction

The chelates of phosphorus-, sulfur- or selenium-containing ligands with coinage metal cations are of great importance due to their photophysical properties,[1,2] application for the creation of chalcogenide nanoparticles,[3] and use as models for biological systems.[4] Therefore, complexes of dithio(seleno)phosphinic acids [RR′P(X)YH] (X, Y = S, Se) and imidodithio(seleno)-diphosphinate ligands [$R_2P(X)NHP(X)R'_2$] (IDP) with coinage metal cations have recently drawn considerable attention.[5–7] There is a growing family of IDP polynuclear aggregates of common formula $[M_3\{R_2P(X)NP(X)R'_2\}_3]$ (**1**) (M = Cu(I), Ag(I); X = S, Se) with a cyclic M_3X_3 core[3a,8,9] and ionic complexes $[M_4\{Ph_2P(X)NP(X)Ph_2\}_3]^+An^-$ (**2**) with a tetrahedral M_4 core surrounded by six chalcogen atoms (Chart 1).[6] Contrary to the previously mentioned ligands, there is a lack of information about structures of the polynuclear copper(I) complexes containing *N*-thiophosphorylated thioureas and thioamides, $RC(S)NHP(S)R'_2$ (**3**) (R = R′$_2$N, Alk, Ar), which are IDP's asymmetrical analogues containing the thiocarbonyl group instead of one thiophosphinic unit. The structures of only two species, a cyclic trimer $[Cu_3\{Et_2NC(S)NP(S)(OPh)_2\}_3]$ (**4**),[10] and an ionic aggregate with unusual "tent-like" structure $[Cu_{10}\{PhNHC(S)NP(S)(OEt)_2\}_9]ClO_4$ (**5**),[11] have been reported.

The IDP ligands have mostly simple substituents R, R′ = Ar, Alk, OAr or OAlk. Presence of the sp^2-carbon atom in the S–C–N–P–Y ligand backbone of (**3**) facilitates modification of the ligands. Multifunctional molecules containing fragments of



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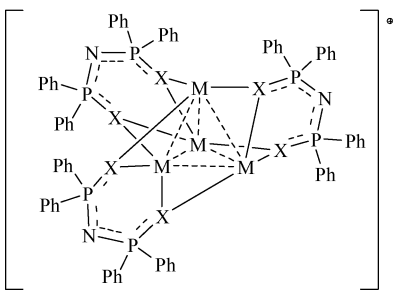

(2)

Chart 1

crown-ethers, aza-macrocycles, *etc.* can be easily obtained.[12,13] It opens interesting perspectives for the further application of these complexes in selective catalysis and crystal engineering.

In this work, we describe the synthesis and the structural characterization of several new polynuclear complexes of the Cu(I) cation with *N*-thiophosphorylthiourea ligands $RC(S)NHP(S)(OiPr)_2$ [R = morpholin-*N*-yl (HL^a), piperidin-*N*-yl (HL^b), NH_2 (HL^c), $PhCH_2NH$ (HL^d)] (Chart 2) and their mononuclear analogues containing triphenylphosphine ligands.

Results and discussion

N-thiophosphorylated thioureas HL^{a-d} were prepared by addition of the corresponding amine to *O*,*O*-diisopropylthiophosphoric acid isothiocyanate $(iPrO)_2P(S)NCS$. Reaction of the potassium salts of HL^{a-d} with $[Cu(PPh_3)_3I]$ in aqueous $EtOH/CH_2Cl_2$ leads to mononuclear $[Cu(PPh_3)_2L^{a-d}]$ complexes (**6a–d**). When

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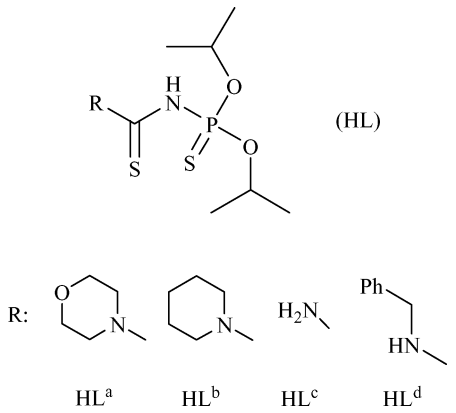
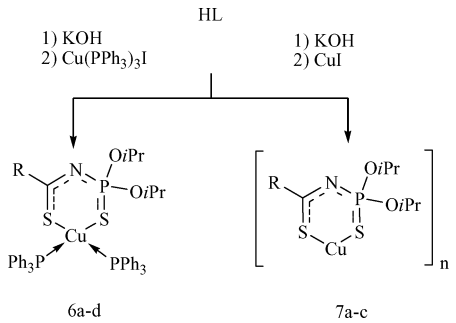


Chart 2

using CuI instead of $Cu(PPh_3)_3I$ polynuclear $[Cu_nL_n^{a-c}]$ complexes (**7a–c**) were formed (Scheme 1). Thiourea HL^b decays when stored for several days, therefore the *one pot* synthesis was used to yield its complexes.



Scheme 1

Reaction of the potassium salt of HL^d with CuI does not lead to stable Cu(I) chelates. It is known that *N*-phosphorylthiourea complexes bearing AlkNH groups easily react with nucleophiles to form phosphorylated guanidines, ureas and isoureas.[13a] The C=N group stretching vibration band at 1600–1650 cm^{-1} in the IR spectra of the reaction mixture and ^{31}P NMR signals in the range of 58–60 ppm confirm the decomposition of the ligand.

The chelates obtained are colourless crystalline powders, soluble in acetone, benzene, dichloromethane and insoluble in water and *n*-hexane. ^1H, $^{31}P\{^1H\}$ NMR in solution and IR data indicated that thioureas HL are 1,5-*S*,*S*′-ligands in all the present cases studied. Conductometric analyses in acetone have shown an absence of conductivity for complexes **6** and **7**.

The ES-MS spectra obtained are similar for all polynuclear complexes of **7**. The strongest peaks correspond to the $[Cu_4L_3]^+$ cations. Mass-spectra also contain the peaks of the $[Cu_3L_3 + Na]^+$ and $[Cu_3L_2]^+$ ions. $[Cu_4L_3]^+$ and $[Cu_3L_2]^+$ species are observed in the spectra of the compounds **6**, however, in these cases the maximum intensity belongs to the peaks of $[Cu(PPh_3)_2]^+$.

The IR spectra of HL contain weak bands centered at 620–676 cm^{-1} assigned to the P=S groups. They are shifted to low frequencies (580–608 cm^{-1}) in the spectra of complexes **6** and **7** due to the coordination with the Cu(I) ion. Occurrence of the new broad and strong absorption peak at 1460–1568 cm^{-1}, related to the conjugated SCN group,[12] also proves the formation of *S*,*S*′-chelates. There are no NH group absorption bands in the IR spectra of the chelates containing anionic forms of $L^{a,b}$. Presence of the NH_2 group in HL^c and its complexes is seen in the IR spectra by its ν_{as}, ν_s and δNH_2 absorption bands. A unique band at 3320 cm^{-1} related to the AlkNH group was observed in the spectrum of **6d**.

The $^{31}P\{^1H\}$ NMR spectra of $HL^{a,b}$ in a $CDCl_3$ solution show a single resonance around 60 ppm. The corresponding ^{31}P resonance in $HL^{c,d}$ is high-field shifted by approximately 6.5 ppm. This difference in the ^{31}P NMR chemical shifts is typical for *N*-thiophosphorylated thioureas with the tertiary amine group R ($HL^{a,b}$) relative to $HL^{c,d}$ ligands containing secondary amine substituents R′NH, where R′ = H, Alk, Ar.[12] In the $^{31}P\{^1H\}$ NMR spectra of mononuclear complexes **6**, the resonances in the range 51.8–55.3 ppm correspond to the phosphorus atoms of the thiophosphoryl group. The signals of triphenylphosphine groups are shifted downfield relative to the free PPh_3 and exhibit ^{31}P NMR chemical shifts at about −1 ppm. In solution, the fast exchange between free and bound triphenylphosphine groups of complexes **6** results in a signal broadening of the $^{31}P\{^1H\}$ NMR spectra, as it was previously observed for the Cu(I) complexes with *N*-thioacylamidothiophosphates.[13] Formation of polynuclear complexes **7a–c** leads to a high-field shift of the ^{31}P resonance of the thiophosphoryl group. For complexes **7a**,**b**, the $^{31}P\{^1H\}$ NMR spectra recorded at 25 and −50 °C show a single narrow peak (fwhm of 3–5 Hz) at around 50 ppm. For **7c** the $^{31}P\{^1H\}$ NMR spectrum, obtained at 25 °C, shows a single slightly-wider resonance in the same region (Fig. 1), while several additional peaks are observed in the low-temperature spectrum. Further analyses are required to unambiguously assign these additional signals. It could be assumed, however, that at low temperature several polynuclear compounds having various structures and different values of *n* occur. The range of observed ^{31}P NMR chemical shifts would suggest that both thiocarbonyl and thiophosphoryl groups form bridging bonds involving sulfur atoms. In the case of complexes **7a**,**b**, steric effects due to the demanding substituents would interfere with such association processes.

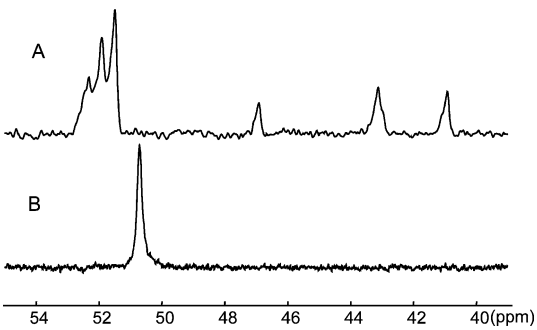


Fig. 1 $^{31}P\{^1H\}$ NMR spectra of $[Cu_n(L^c)_n]$ (**7c**) (−50 °C (A), 25 °C (B)) in $CDCl_3$.

The ^1H NMR spectra of complexes **6** and **7** in $CDCl_3$ contain the signals expected for the proposed structure only (chemical shifts and *J*-coupling constants are given in the Experimental section). The ^1H signal of the NHP(S) group is absent in the ^1H NMR spectra, confirming the anionic form of L^{a-d}.

In the ^1H NMR spectrum of HL^c, the signals of the two nonequivalent protons of the NH_2 group are observed. These two ^1H resonances are also evidenced in the ^1H NMR low-temperature

spectrum (−50 °C) of the **6c** complex. The downfield shift of the H_b proton of **6c**, observed at low temperature (Fig. 2B) is caused by the intermolecular H-bonding in solution. The spectrum of **6c**, recorded at 25 °C, exhibits a motional-averaged signal of the NH_2 group with an intensity corresponding to two protons (see Fig. 2A and 2B). This is caused by dissociation of the weak intermolecular H-bonds and a decrease in the H_2N–C bond rotation barrier at the higher temperature.

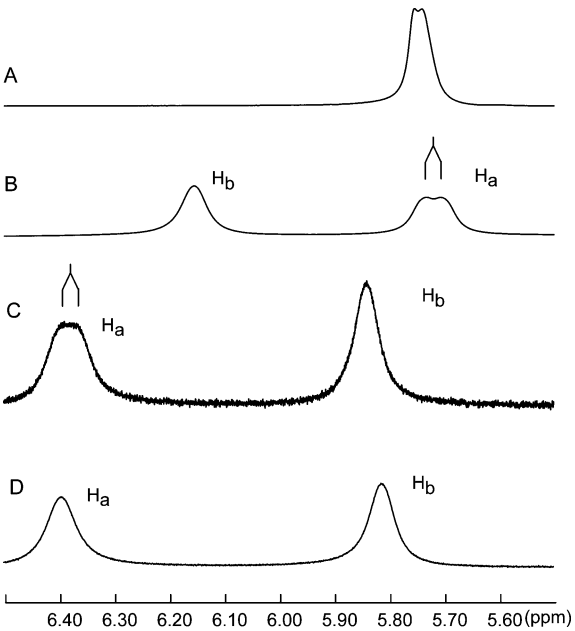


Fig. 2 NH_2 group proton resonance of complexes $[Cu(PPh_3)_2L^c]$ (**6c**) at 25 °C (A), −50 °C (B), and $[Cu_nL_n^c]$ (**7c**) at 25 °C (C) in $CDCl_3$ without (C), and with (D) phosphorus decoupling.

It should be noted that the signals of the H_a and H_b protons of the NH_2 groups in **6c** and **7c** have different scalar coupling with the phosphorus atom (Chart 3). The high-field resonance of the NH_2 group in **6c** clearly shows a splitting due to the $^4J_{PNCNH}$ spin–spin interaction. Similar splitting is observed for the downfield NH_2 signal in **7c**. Rather high $^4J_{PNCNH}$ coupling constants are measured for mononuclear **6c** (7.7 Hz) and polynuclear **7c** (8.6 Hz) complexes. This was previously reported for other *N*-phosphorylthiourea complexes[13,14] and attributed to the fact that the P–N–C–N–H chain matches the so-called *W*-criterion (Chart 3).[15] The contribution of the observed splitting to the presence of $^4J_{PNCNH}$ spin–spin coupling was unambiguously confirmed by recording ^1H NMR spectra with ^{31}P decoupling (*e.g.* Fig. 2D).

For complex **7c** in $CDCl_3$, a comparative analysis of ^1H NMR data gives evidence for the existence of a polynuclear chelate at room temperature. The ^1H NMR spectrum, obtained at 25 °C, shows two signals of equal intensity corresponding to the two nonequivalent protons of the NH_2 group (Fig. 2C). This is explained by the participation of the sulfur atom of the C=S groups in the bridging bonds resulting in a decrease of the electronic density in the conjugated chelate cycle and, hence, to the increase of the conjugation degree of the lone electron pair of the NH_2 group and an increase of the H_2N–C bond rotation barrier.

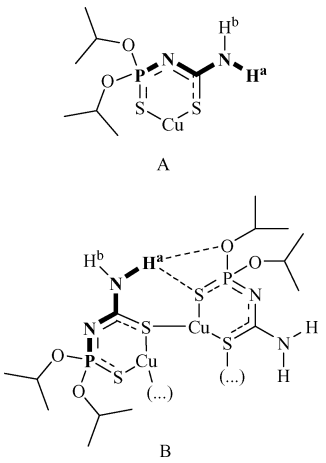


Chart 3

Variation of the chemical shift for the H^a proton of the NH_2 group in complexes **6c** and **7c** could be assigned to the formation of intramolecular hydrogen bonds in molecules of the polynuclear aggregate (Chart 3B). This is confirmed by the ^1H NMR spectrum of **7c** in d_6-acetone which shows a weak shift of the H^a resonance ($\Delta\delta_H$ + 0.3 ppm) whereas the H^b peak is strongly downfield shifted ($\Delta\delta_H$ + 1.5) due to the formation of hydrogen bonds with the solvent.

Thus, comparative analysis of the ^1H NMR spectra of the NH_2 moieties in **6c** and **7c** clearly demonstrates the preservation of the bonding between $[CuL^c]$ units of $[Cu_nL_n^c]$ aggregates in a $CDCl_3$ solution.

Crystal structures of mononuclear **6b** and trimeric **7a** complexes were determined by single crystal X-ray diffraction. The complexes obtained have been crystallized from dichloromethane–*n*-hexane solution, 1 : 2 (v/v). In the structure of **6b** (Fig. 3), the copper(I) cation is in a P_2S_2 tetrahedral environment. The weak distortions relative to a perfect tetrahedron (Table 1) reveal the absence of major steric hindrance. According to the X-ray data, complex **7a** is a cyclic trimer (Fig. 4), in which the Cu–S–Cu bridging

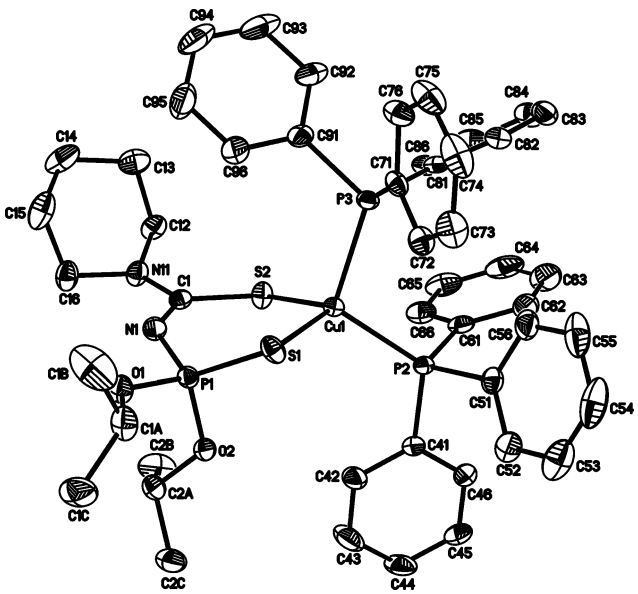


Fig. 3 Molecular structure of complex $[Cu(PPh_3)_2L^b]$ (**6b**).

Table 1 Selected bond lengths, bond angles, and torsion angles for complex $[Cu(PPh_3)_2L^b]$ (**6b**)

Bond lengths/Å			
C(1)–S(2)	1.746(2)	Cu(1)–P(2)	2.2970(6)
C(1)–N(1)	1.325(3)	Cu(1)–P(3)	2.3162(6)
C(1)–N(11)	1.364(3)	Cu(1)–S(1)	2.3479(6)
N(1)–P(1)	1.590(2)	Cu(1)–S(2)	2.3051(6)
P(1)–S(1)	1.9821(8)		
Bond angles/°			
S(1)–Cu(1)–S(2)	109.19(2)	P(2)–Cu(1)–P(3)	110.12(2)
Torsion angles/°			
S(1)–P(1)–N(1)–C(1)	53.8(2)		

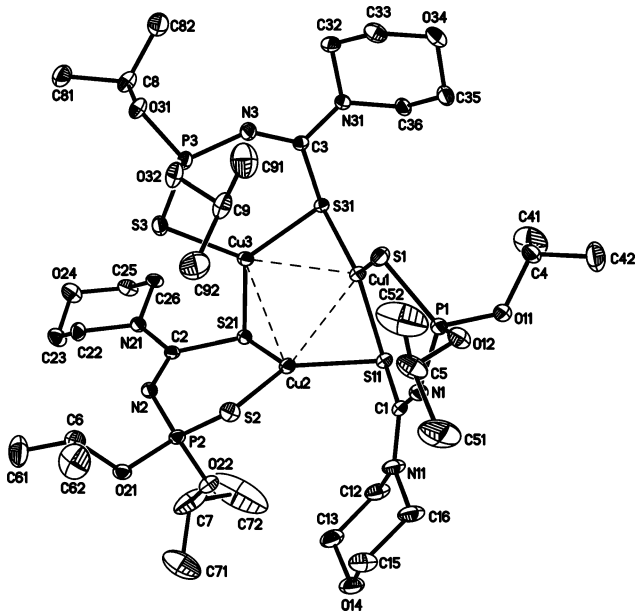


Fig. 4 Molecular structure of complex $[Cu_3L_3^a]$ (**7a**).

bonds are formed by the sulfur atoms of the C=S groups. The Cu_3S_3 cyclic backbone is in a chair conformation and the copper atoms are in a S_3 trigonal-planar environment. In the crystal structure, the molecular unit is distorted and does not possess a C_3 symmetry axis. The distances Cu(1)–Cu(2) 2.8546(4) and Cu(2)–Cu(3) 2.7614(3) indicate lack of any distinct Cu–Cu interactions[11] and the Cu(1)–Cu(3) distance is the longest one (3.0789 Å). This variation in the Cu–Cu distances leads to an increase of the Cu(1)–S(31)–Cu(3) bond angle relative to the Cu(1)–S(11)–Cu(2) and Cu(2)–S(21)–Cu(3) angles (Table 2). The cyclic Cu(1)–S(11)–C(1)–N(1)–P(1)–S(1) moiety is almost flat. The Cu(2)–S(21)–C(2)–N(2)–P(2)–S(2) and Cu(3)–S(31)–C(3)–N(3)–P(3)–S(3) six-membered chelate rings are similar to that in the mononuclear analogue **6b** which adopts a distorted boat conformation with the maximal distortion of the thiophosphoryl sulfur atoms from the N–C(S)–N–P–O plane. In these chelate rings, the C–S and P–S bonds are lengthened, while C–N and P–N bonds are shortened (Table 2) in comparison to the typical values for *N*-thiophosphorylated thioureas and thioamides.[12] In

Table 2 Selected bond lengths, bond angles, and torsion angles for complex $[Cu_3L_3^a]$ (**7a**)

Bond lengths/Å			
Cu(1)–S(31)	2.2443(5)	P(3)–N(3)	1.593(2)
Cu(1)–S(11)	2.2469(5)	Cu(3)–S(31)	2.2032(5)
Cu(1)–S(1)	2.2507(6)	Cu(3)–S(3)	2.2406(6)
S(11)–Cu(2)	2.2634(5)	S(1)–P(1)	1.9899(7)
Cu(2)–S(21)	2.2437(5)	P(1)–N(1)	1.604(2)
Cu(2)–S(2)	2.2624(6)	N(1)–C(1)	1.307(3)
S(21)–Cu(3)	2.2653(5)	C(1)–S(11)	1.787(2)
P(2)–N(2)	1.610(2)	S(2)–P(2)	1.9847(7)
N(2)–C(2)	1.312(2)	N(3)–C(3)	1.308(2)
C(2)–S(21)	1.786(2)	C(3)–S(31)	1.791(2)
S(3)–P(3)	1.9950(8)		
Bond angles/°			
Cu(1)–S(11)–Cu(2)	78.53(2)		
Cu(2)–S(21)–Cu(3)	75.53(2)		
Cu(3)–S(31)–Cu(1)	87.62(2)		
Torsion angles/°			
S(1)–P(1)–N(1)–C(1)	53.8(2)		
S(3)–P(3)–N(3)–C(3)	−27.8(3)		
S(2)–P(2)–N(2)–C(2)	58.1(2)		

the polynuclear complex **7a**, the C–S bonds, participating in the formation of bridges, are especially strongly lengthened to the values 1.787(2), 1.7858(18) and 1.7910(18) Å characteristic for single bonds.[16]

The data presented clearly show that increasing the coordination number of the thiocarbonyl sulfur atoms in polynuclear chelates **4**, **5**, **7a** leads to a lengthening of the CS and CN bonds and a shortening of the Cu–S bonds in comparison with the mononuclear analog **6b**. In our opinion, it could be caused by the more effective overlap of copper(I) and sulfur orbitals in the CuS_3 and CuS_4 environments than in the CuP_2S_2 complex core.

Comparison of polynuclear complexes **4**, **5**, **7a** shows, that the conjugated SCNPS moiety in the ligand anions possesses sufficient structural flexibility due to the presence of the phosphorus atom in it. A low rotation barrier around the PN bond in the chelate cycles provides realization of various types of the folded conformations.[10,11]

Thiocarbonyl and thiophosphoryl sulfur atoms are capable to form bridging bonds between the [CuL] units. However, the ability of such association essentially depends on the structure of the substituents at the chelate units. The lack of experimental data means a law of such aggregates formation can not be formulated at the moment. However, it is possible to assume that a reduction of the sterical demands at the chetate unit facilitates increasing the coordination numbers of the sulfur and copper(I) atoms. The increase in association degree in the aggregates **5** and **7c** confirms this assumption.

The structures of the crystalline mononuclear **6a–c** and polynuclear **7a–c** complexes were also characterized by ^{31}P solid-state magic angle spinning (MAS) NMR spectroscopy.

According to the X-ray data, there are four equivalent molecules in the asymmetric unit of the mononuclear complex **6b**, each of them containing three crystallographically inequivalent P sites.

The $^{31}P\{^{1}H\}$ CPMAS spectra with ^{1}H decoupling is in agreement with the X-ray diffraction data (Fig. 5A). In this spectrum, the resonance of the P atom of the thiophosphoryl group appears as a single peak with a ^{31}P NMR chemical shift of −52.8 ppm, while the two inequivalent triphenylphosphine P sites give rise to four multiplets owing to the direct *J*-couplings with the ^{63}Cu and ^{65}Cu isotopes. These multiplets appear as a quadruplet ($^{63,65}Cu$, I = 3/2) of doublets due to the presence of a homonuclear $^{2}J_{PCuP}$ coupling of about 98 Hz, which was also measured using a two-dimensional spin echo MAS experiment[17–19] (not shown). These $^{1}J_{PCu}$ and $^{2}J_{PCuP}$ couplings were not observed in the solution NMR spectra due to the fast exchange between free and bound triphenylphosphine groups. Table 3 gives the ^{31}P NMR isotropic chemical shifts and isotropic *J*-coupling constants determined from the simulations of the CPMAS spectra. The coupling constants obtained are comparable to values found previously for complexes with the same complex core CuP_2S_2,[20] but slightly smaller because of longer Cu–P bond distances. The P-site quantification obtained from a single pulse spectrum is in agreement with the expected multiplicities and the $^{63,65}Cu$ isotopic abundances. The simulation of the *J*-multiplet patterns takes into account "residual dipolar" effects due to the dipolar and anisotropic scalar couplings between ^{31}P and the quadrupolar copper nucleus.[21–23] However, only the magnitude of this term was fitted since both the $^{63,65}Cu$ quadrupolar coupling constants and *J*-coupling anisotropy are unknown. The $^{31}P\{^{1}H\}$ CPMAS spectra of the mononuclear complex **6a** is shown in Fig. 5B, As for **6b**, this spectrum shows a single resonance for the thiophosphoryl group and four partly overlapping quadruplets of doublets for the triphenylphosphine groups, indicating that the crystal structure of this complex contains one distinct molecular unit with three inequivalent P sites. For mononuclear complex **6a**, the ^{31}P isotropic chemical shifts and *J*-coupling constants are very similar to those measured for **6b**. The spectrum of **6c** shows a single narrow resonance for the thiophosphoryl group (Fig. 5C). However, the complex *J*-multiplet patterns of the triphenylphosphine resonances are not resolved and only a broad asymmetric quadruplet is observed. The lack of the spectral resolution could be due to a more pronounced "residual dipolar effect", which would arise from a very large $^{63,65}Cu$ quadrupolar coupling constant and would result in a second order broadening of the ^{31}P *J*-multiplets.[21–23] In order to get a more detailed interpretation of this spectrum, additional $^{63,65}Cu$ and ^{31}P NMR experiments at very high magnetic fields are in progress.

The $^{31}P\{^{1}H\}$ CPMAS spectra of polynuclear copper(I) complexes **7** are also shown in Fig. 5. In the case of **7a**, the spectrum contains three resolved resonances at 45.4, 52.8 and 53.4 ppm with relative intensities in the ratio ~1 : 1 : 1, corresponding to the three crystallographically inequivalent PS groups per molecule, in agreement with the X-ray diffraction data. The $^{31}P\{^{1}H\}$ CPMAS spectrum of **7b** (Fig. 5E) exhibits two partly resolved peaks with an

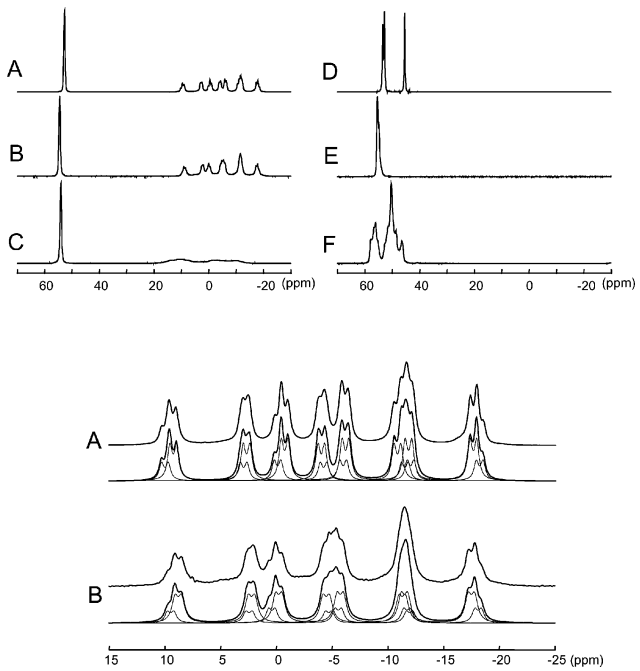


Fig. 5 $^{31}P\{^{1}H\}$ solid state CPMAS NMR spectra of mononuclear complexes $[Cu(PPh_3)_2L]$ **6b** (A), **6a** (B), **6c** (C) and polynuclear complexes $[Cu_nL_n]$ **7a** (*n* = 3) (D), **7b** (E), **7c** (F) (top). Expansion of the experimental and simulated *J*-multiplet patterns of the mononuclear samples (A) and (B) (bottom).

Table 3 ^{31}P isotropic chemical shifts and $^{1}J_{P\text{–}Cu}$ and $^{2}J_{P\text{–}P}$ coupling constants of Cu(I) complexes. Estimation of errors according to *Dmfit* 2007 is ±6 Hz. (nm: not measured)

Complex	P site	δ_{iso} (ppm)	$^{1}J(^{63}Cu\text{–}^{31}P)$/Hz	$^{1}J(^{65}Cu\text{–}^{31}P)$/Hz	$^{2}J(^{31}P\text{–}^{31}P)$/Hz	*I* (%)
6a	$[PPh_3]$	−8.6	933	999	94	30.2
	$[PPh_3]$	−1.1	1082	1158	94	33.8
	[CuL]	54.5				36.0
6b	$[PPh_3]$	−9.0	913	978	98	35.3
	$[PPh_3]$	−0.7	1085	1161	98	33.4
	[CuL]	52.8				31.3
6c	[CuL]	−8.6				39.4
	$[PPh_3]$	nm	nm	nm	nm	60.6
7a	[CuL]	45.4				33.4
	[CuL]	52.8				31.9
	[CuL]	53.4				34.7
7c	[CuL]	54.9				32.5
	[CuL]	55.5				67.5

intensity ratio 2 : 1. In this spectrum, the most intense peak shows a slightly asymmetric lineshape that would suggest the presence of two overlapping resonances. This spectrum would therefore be consistent with the presence of three inequivalent P sites, two of them having very similar ^{31}P NMR isotropic chemical shifts and with the formation of a trimeric associate [$Cu_3L_3^b$]. For **7c**, the ^{31}P CPMAS spectrum is much more complex and exhibits at least 8 partly overlapping thiophosphoryl resonances with different relative intensities. In this case, the ^{31}P NMR spectrum could indicate the presence of several polynuclear complexes having different *n* values and/or the presence of different isomeric structures.

Conclusions

Reaction of [$Cu(PPh_3)_3I$] with the potassium salts of the *N*-thiophosphorylated thioureas HL^{a-d} has allowed us to obtain complexes of composition [$Cu(PPh_3)_2L$] (**6a–d**) containing tetracoordinated atoms of copper(I). A similar reaction using CuI instead of [$Cu(PPh_3)_3I$] yields the [Cu_nL_n] polynuclear analogues **7a–c**. NMR experiments in solution and IR have shown that HL^{a-d} are 1,5-*S*,*S*′-ligands in all cases.

Crystal structures of mononuclear **6b** and polynuclear **7a** complexes were determined by single crystal X-ray diffraction. According to the X-ray data, [$Cu_3L_3^a$] (**7a**) is a cyclic trimer, formed by the bridging bonds with participation of the thiocarbonyl sulfur atoms. Additionally ^{31}P solid state NMR experiments indicate the formation of the polynuclear associate [$Cu_nL_n^b$] (**7b**) with $n = 3$, while for [$Cu_nL_n^c$] (**7c**) the ^{31}P NMR spectrum suggests the formation of several polynuclear complexes having different *n* values and/or different isomeric structures.

Experimental

General procedures

Tris-triphenylphosphine copper(I) iodide [$Cu(PPh_3)_3I$] was synthesised using a previously described method.[24] Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyser. Electrospray ionization mass spectra were measured with a Finnigan-Mat TCQ 700 mass spectrometer on a 10^{-6} M solution in CH_3OH. The speed of sample submission was 2 μL min^{-1}. The ionization energy was 4.5 kV and the capillary temperature was 200 °C. Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the frequency range 400–3600 cm^{-1}. ^{1}H and ^{31}P NMR experiments in solution were performed on a Bruker AMX-300 NMR spectrometer. ^{31}P NMR spectra with continuous wave ^{1}H decoupling were acquired using a single pulse of 7 μs duration (π/4) and a recycle delay varying between 1 to 5 s to ensure no saturation. ^{31}P solid-state magic angle spinning (MAS) NMR were carried out on a Bruker Avance 400 (9.4 T) spectrometer using a 4 mm probe-head. The ^{31}P{^{1}H} cross-polarization (CP) MAS NMR spectra were recorded at a spinning frequency of 14 kHz using a ramped cross-polarization[25] with a contact time of 1 ms and a recycle delay of 2 s. ^{1}H decoupling was achieved using the SPINAL-64 sequence[26] with a ^{1}H nutation frequency of about 60 kHz. Quantitative MAS spectra were acquired (with and without ^{1}H decoupling) using a single pulse of 0.5 μs duration (π/12) and a recycle delay of 1 s. Chemical shifts are referred to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P) solutions. All MAS NMR spectra were modeled using the *Dmfit* program.[27]

Synthesis of HL^a. A solution of morpholine (1.044 g, 12 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of $SCNP(S)(OiPr)_2$ (3.155 g, 13.2 mmol) in the same solvent (15 mL). The mixture was stirred at room temperature for 3 h. The solvent was then removed in vacuum. The residue was recrystallized from a dichloromethane–*n*-hexane mixture 1 : 5 (v/v). The product was obtained as colorless crystals. Yield: 3.129 g, 80%. mp = 84 °C. ^{1}H NMR (d_6-acetone) 1.31 (d, $^3J_{H,H}$ = 6.0 Hz, 12H, CH_3), 3.66 (m, 4H, OCH_2), 3.89 (m, 4H, NCH_2), 4.87 (d. sept, $^3J_{POCH}$ = 10.9 Hz, $^3J_{H,H}$ = 6.0 Hz, 2H, OCH), 6.06 (br. s, 1H, NH) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$) 59.5 ppm; ^{31}P{^{1}H} NMR (d_6-acetone) 61.5 ppm; IR (cm^{-1}): 3232 (NH), 1496 (S=C–N), 1112 (COC), 960, 1000,1040 (POC), 623 (P=S). Anal. Calcd for $C_{11}H_{23}N_2O_3PS_2$ (326.42): C, 40.48; H, 7.10; N, 8.58. Found: C, 40.41; H, 7.06; N, 8.60.

HL^b. This was prepared similar to that described for HL^a but with piperidine (1.020 g, 12 mmol). The product was obtained as colorless crystals. Yield: 3.499 g, 90%. mp = 101 °C. ^{1}H NMR ($CDCl_3$) 1.36 (br. s, 12H, CH_3), 1.65 (br. s, 6H, β,γ-CH_2, *c*-$C_5H_{10}N$), 3.81 (br. s, 4H, α-CH_2, *c*-$C_5H_{10}N$), 4.89 (br. s, 2H, OCH), 5.93 (br. s, 1H, NH) ppm; ^{31}P{^{1}H} NMR ($CDCl_3$) 59.9 ppm; IR (cm^{-1}): 3200 (NH), 1502 (S=C–N), 1000,1008 (POC), 624 (P=S). Anal. Calcd for $C_{12}H_{25}N_2O_2PS_2$ (324.44): C, 44.42; H, 7.77; N, 8.63. Found: C, 44.45; H, 7.73; N, 8.59.

HL^c. This was prepared similar to that described for HL^a but with a 30% water solution of ammonia (0.680 g, 12 mmol). The product was obtained as colorless crystals.[28] Yield: 2.673 g, 87%. mp = 111 °C. ^{1}H NMR ($CDCl_3$) 1.33 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3), 4.78 (d. sept, $^3J_{POCH}$ = 10.5 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH), 4.91 (d, $^2J_{HNP}$ = 10.1 Hz, 1H, NH), 7.03 (s, 1H, NH_2), 7.55 (s, 1H, NH_2) ppm; ^{31}P{^{1}H} NMR (t = 25 °C, $CDCl_3$) 53.3 ppm; ^{31}P{^{1}H} NMR (*t* = −50 °C, $CDCl_3$) 53.1 ppm; IR (cm^{-1}): 3208, 3180, 3060 (NH + NH_2), 1628 (NH_2), 1492 (S=C–N), 976 (POC), 676 (P=S). Anal. Calcd for $C_7H_{17}N_2O_2PS_2$ (256.33): C, 32.80; H, 6.68; N, 10.93. Found: C, 32.81; H, 6.62; N, 10.88.

HL^d. This was prepared similar to that described for HL^a but with benzylamine (1.284 g, 12 mmol). The product was obtained as colorless crystals. Yield: 3.446 g, 83%. mp = 125 °C. ^{1}H NMR (CCl_4 + C_6D_6) 1.36 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_3), 1.38 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_3), 4.86 (d. sept, $^3J_{POCH}$ = 10.7 Hz, $^3J_{H,H}$ = 6.4 Hz, 2H, OCH), 4.91 (d, $^3J_{HCNH}$ = 5.4 Hz, 2H, CH_2), 7.32–7.44 (m, 5H, C_6H_5), 8.32 (s, 1H, NHP), 8.49 (t, $^3J_{HCNH}$ = 4.9 Hz, 1H, NH) ppm; ^{31}P{^{1}H} NMR (CCl_4 + C_6D_6) 53.0 ppm; IR (cm^{-1}): 3255, 3070 (NH), 1548 (S=C–N), 980 (POC), 620 (P=S). Anal. Calcd for $C_{14}H_{23}N_2O_2PS_2$ (346.45): C, 48.54; H, 6.69; N, 8.04. Found: C, 48.51; H, 6.72; N, 8.08.

Synthesis of [$Cu(PPh_3)_2L^a$] (6a). A suspension of HL^a (0.978 g, 3 mmol) in aqueous ethanol (25 mL) was mixed with an ethanol solution of KOH (0.185 g 3.3 mmol). A dichloromethane (25 mL) solution of [$Cu(PPh_3)_3I$] (2.931 g, 3 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further hour and a precipitate was filtered off. The filtrate was concentrated until the crystallization began. The residue was recrystallized from a

dichloromethane–*n*-hexane mixture 1 : 5 (v/v). Complex **6a** was obtained as colorless crystals. Yield: 1.917 g, 70%. mp = 151 °C. ^{1}H NMR ($CDCl_3$) 1.26 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3), 1.31 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3), 3.60–3.74 (m, 4H, OCH_2), 3.80–4.22 (m, 4H, NCH_2), 4.71 (d. sept, $^3J_{POCH}$ = 10.8 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH), 7.27–7.43 (m, 30H, C_6H_5) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) −1.2 (PPh_3), 53.3 (L) ppm; IR (cm^{-1}): 1460 (SCN), 1100 (COC), 960, 1015 (POC), 598 (P=S). ES-MS (positive ion): *m*/*z* (%) = 1230 (28) $[Cu_4L_3]^+$, 1189 (1) $[Cu_3L_3 + Na]^+$, 841 (5) $[Cu_3L_2]^+$, 589 (100) $[Cu(PPh_3)_2]^+$. Anal. Calcd for $C_{47}H_{52}CuN_2O_3P_3S_2$ (913.52): C, 61.79; H, 5.74; N, 3.07. Found: C, 61.81; H, 5.78; N, 3.02.

Synthesis of [Cu(PPh$_3$)$_2$L^b] (6b). A solution of piperidine (0.507 g, 5.9 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of SCNP(S)(O*i*Pr)$_2$ (1.410 g, 5.9 mmol) in CH_2Cl_2 (20 mL) under vigorous stirring. After 3 h, the solution was removed in vacuum and a potassium hydroxide solution (0.364 g, 6.5 mmol) in aqueous ethanol (20 mL) was added to the residue and the mixture was stirred until the ligand was completely dissolved. The steps which follow are similar to those used in the synthesis of **6a**. Complex **6b** was obtained as colorless crystals. Yield: 3.228 g, 60%. mp = 137 °C. ^{1}H NMR ($CDCl_3$) 1.26 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3), 1.30 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3), 1.50–1.67 (m, 6H, CH_2), 3.75–3.90 (m, 2H, NCH_2), 4.00–4.15 (m, 2H, NCH_2), 4.71 (d. sept, $^3J_{POCH}$ = 10.8 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH), 7.28–7.44 (m, 30H, C_6H_5) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) −0.9 (PPh_3), 51.8 (L) ppm; IR (cm^{-1}): 1485 (SCN), 980, 1010 (POC), 590 (P=S). ES-MS (positive ion): *m*/*z* (%) = 837 (56) $[Cu_3L_2]^+$, 712 (15) $[CuL_2 + 2H]^+$, 651 (33) $[Cu(PPh_3)L + H]^+$, 589 (100) $[Cu(PPh_3)_2]^+$, 387 (24) $[CuL + H]^+$. Anal. Calcd for $C_{48}H_{54}CuN_2O_2P_3S_2$ (911.55): C, 63.25; H, 5.97; N, 3.07. Found: C, 63.21; H, 6.01; N, 3.08.

[Cu(PPh$_3$)$_2$L^c] (6c). was prepared similar to that described for **6a** but with HL^c (0.768 g, 3 mmol). Complex **6c** was obtained as colorless crystals. Yield: 2.074 g, 82%. mp = 119 °C. ^{1}H NMR ($CDCl_3$) 1.27 (d, $^3J_{H,H}$ = 6.1 Hz, 6H, CH_3), 1.28 (d, $^3J_{H,H}$ = 6.1 Hz, 6H, CH_3), 4.70 (d. sept, $^3J_{POCH}$ = 10.6 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH), 5.72 (br. s, 2H, NH_2), 7.24–7.39 (m, 30H, C_6H_5) ppm; $^{31}P\{^1H\}$ NMR (*t* = 25 °C, $CDCl_3$) −0.7 (PPh_3), 55.3 (L) ppm; $^{31}P\{^1H\}$ NMR (t = −50 °C, $CDCl_3$) −2.8 (PPh_3), 57.8 (L) ppm; IR (cm^{-1}): 3504, 3256, 3120, 1610 (NH_2), 1520 (SCN), 1000 (POC), 608 (P=S). ES-MS (positive ion): *m*/*z* (%) = 1021 (50) $[Cu_4L_3]^+$, 701 (23) $[Cu_3L_2]^+$, 589 (100) $[Cu(PPh_3)_2]^+$. Anal. Calcd for $C_{43}H_{46}CuN_2O_2P_3S_2$ (843.43): C, 61.23; H, 5.50; N, 3.32. Found: C, 61.26; H, 5.47; N, 3.38.

[Cu(PPh$_3$)$_2$L^d] (6d). was prepared similar to that described for **6a** but with HL^d (1.038 g, 3 mmol). Complex **6d** was obtained as colorless crystals. Yield: 2.186 g, 78%. mp = 110 °C. ^{1}H NMR ($CDCl_3$) 1.24 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3), 1.29 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3), 4.53 (d, $^3J_{H,H}$ = 5.5 Hz, 2H, CH_2), 4.69 (d. sept, $^3J_{POCH}$ = 10.7 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH), 6.17 (d. t, $^4J_{PNCNH}$ = 8.2 Hz, $^3J_{H,H}$ = 5.5 Hz, 1H, NH), 7.23–7.41 (m, 35H, C_6H_5) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) −0.9 (PPh_3), 54.9 (L) ppm; IR (cm^{-1}): 3320 (NH_2), 1530 (SCN), 990, 1010, 1030 (POC), 580 (P=S). ES-MS (positive ion): *m*/*z* (%) = 1290 (24) $[Cu_4L_3]^+$, 881 (5) $[Cu_3L_2]^+$, 672 (22) $[Cu(PPh_3)L + L]^+$, 589 (100) $[Cu(PPh_3)_2]^+$, 410 (18) $[CuL + H]^+$. Anal. Calcd for $C_{50}H_{52}CuN_2O_2P_3S_2$ (933.56): C, 64.33; H, 5.61; N, 3.00. Found: C, 64.36; H, 5.57; N, 3.05.

Synthesis of [Cu$_3$L$_3^a$] (7a). A suspension of HL^a (0.978 g, 3 mmol) in aqueous ethanol (25 mL) was mixed with an ethanol solution of KOH (0.185 g, 3.3 mmol). The resulting mixture was added dropwise to a suspension of CuI (0.570 g, 3 mmol) in aqueous ethanol (20 mL). The mixture was stirred at room temperature for 1.5 h. The resulting precipitate of KI was filtered and the solvent was then removed in vacuum. The residue was recrystallized from a dichloromethane–*n*-hexane mixture 1 : 5 (v/v). Complex **7a** was obtained as light yellow crystals. Yield: 2.605 g, 72%. mp = 140 °C. ^{1}H NMR ($CDCl_3$) 1.30 (d, $^3J_{H,H}$ = 6.2 Hz, 36H, CH_3), 3.66–3.75 (m, 12H, OCH_2), 3.82–3.87 (m, 6H, NCH_2), 4.13–4.17 (m, 6H, NCH_2), 4.67 (d. sept, $^3J_{POCH}$ = 10.6 Hz, $^3J_{H,H}$ = 6.2 Hz, 6H, OCH) ppm; $^{31}P\{^1H\}$ NMR (t = 25 °C, $CDCl_3$) 50.1 ppm; $^{31}P\{^1H\}$ NMR (*t* = −50 °C, $CDCl_3$) 50.7 ppm; IR (cm^{-1}): 1520 (SCN), 1084 (COC), 980, 1000, 1020 (POC), 602 (P=S). ES-MS (positive ion): *m*/*z* (%) = 1230 (100) $[Cu_4L_3]^+$, 1189 (21) $[Cu_3L_3 + Na]^+$, 841 (69) $[Cu_3L_2]^+$. Anal. Calcd for $C_{33}H_{66}Cu_3N_6O_9P_3S_6$ (1166.86): C, 33.97; H, 5.70; N, 7.20. Found: C, 33.92; H, 5.66; N, 7.15.

[Cu$_n$L$_n^b$] (7b). A solution of piperidine (0.507 g, 5.9 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of SCNP(S)(O*i*Pr)$_2$ (1.410 g, 5.9 mmol) in the same solvent (20 mL) under vigorous stirring. After 3 h, the solution was removed in vacuum and a potassium hydroxide (0.364 g, 6.5 mmol) solution in aqueous ethanol (20 mL) was added to the residue and the mixture was stirred until the ligand dissolved completely. The following steps are similar to those used in the synthesis of **7a**. Complex **7b** was obtained as yellow crystals. Yield: 1.911 g, 84% ([CuL^b] relative to SCNP(S)(O*i*Pr)$_2$). mp = 133 °C. ^{1}H NMR ($CDCl_3$) 1.29 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3), 1.52–1.71 (m, 6H, CH_2), 3.75–3.85 (m, 2H, NCH_2), 4.05–4.15 (m, 2H, NCH_2), 4.68 (d. sept, $^3J_{POCH}$ = 10.6 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, OCH) ppm; $^{31}P\{^1H\}$ NMR (*t* = 25 °C, $CDCl_3$) 48.9 ppm; $^{31}P\{^1H\}$ NMR (*t* = −50 °C, $CDCl_3$) 49.3 ppm; IR (cm^{-1}): 1510 (SCN), 990, 1010, 1020 (POC), 595 (P=S). ES-MS (positive ion): *m*/*z* (%) = 1225 (100) $[Cu_4L_3]^+$, 1185 (12) $[Cu_3L_3 + Na]^+$, 837 (56) $[Cu_3L_2]^+$. Anal. Calcd for $C_{12}H_{24}CuN_2O_2PS_2$ ([CuL^b], 386.98): C, 37.24; H, 6.25; N, 7.24. Found: C, 37.17; H, 6.26; N, 7.28.

[Cu$_n$L$_n^c$] (7c). was prepared similar to that described for **7a** but with HL^c (1.307 g, 5.1 mmol). Complex **7c** was obtained as beige crystals. Yield: 1.213 g, 75% ([CuL^c] relative to HL^c). mp = 151–153 °C. ^{1}H NMR ($CDCl_3$) 1.34 (d, $^3J_{H,H}$ = 6.4 Hz, 12H, CH_3), 4.73 (d. sept, $^3J_{POCH}$ = $^3J_{H,H}$ = 6.0 Hz, 2H, OCH), 5.84 (br. s, 1H, H_b, NH_2), 6.42 (br. d, $^4J_{PNCNH}$ = 8.6 Hz, 1H, H_a, NH_2) ppm; ^{1}H NMR (d_6-acetone) 1.30 (t, $^3J_{H,H}$ = 6.0 Hz, 12H, CH_3), 4.72 (d. sept, $^3J_{POCH}$ = 10.7 Hz, $^3J_{H,H}$ = 6.1 Hz, 2H, OCH), 6.70 (d, $^4J_{PNCNH}$ = 9.8 Hz, 1H, H_a, NH_2), 7.31 (s, 1H, H_b, NH_2) ppm; $^{31}P\{^1H\}$ NMR (t = 25 °C, $CDCl_3$) 50.7 ppm; $^{31}P\{^1H\}$ NMR (*t* = −50 °C, $CDCl_3$) 40.9, 43.1, 46.9, 51.5, 51.9, 52.3 ppm; $^{31}P\{^1H\}$ NMR (*t* = 25 °C, d_6-acetone) 52.4 ppm; IR (cm^{-1}): 3445, 3280, 3160, 1628 (NH_2), 1568, 1504 (SCN), 1000 (POC), 595 (P=S). ES-MS (positive ion): *m*/*z* (%) = 1021 (100) $[Cu_4L_3]^+$, 701 (16) $[Cu_3L_2]^+$. Anal. Calcd for $C_7H_{16}CuN_2O_2PS_2$ ([CuL^c], 318.86): C, 26.37; H, 5.06; N, 8.79. Found: C, 26.33; H, 5.09; N, 8.72.

X-Ray crystallography

X-Ray crystal structure determination was carried out using a Stoe-IPDS-II two-circle diffractometer with graphite-monochromated Mo-Kα radiation. An empirical absorption correction was performed. The structures were solved by direct methods and refined with full-matrix least-squares on F^2. Hydrogen atoms were placed on ideal positions, and refined with fixed isotropic displacement parameters using a riding model.

Crystal data for 6b. $C_{48}H_{54}CuN_2O_2P_3S_2$, $M_r = 911.50$ g mol^{-1}, colorless prisms, monoclinic, space group $P2_1/n$, $a = 12.9095(7)$, $b = 21.2619(8)$, $c = 17.5378(9)$ Å, $\beta = 109.403(4)°$, $V = 4540.4(4)$ Å^3, $Z = 4$, $\rho = 1.333$ g cm^{-3}, μ(Mo-Kα) = 0.719 mm^{-1}, reflections: 51 935 collected, 8369 unique, $R_{int} = 0.0623$, R_1(all) = 0.0482, wR_2(all) = 0.0806.

Crystal data for 7a. $C_{33}H_{66}Cu_3N_6O_9P_3S_6$, $M_r = 1166.81$ g mol^{-1}, colorless prisms, triclinic, space group P-1, $a = 10.4622(5)$, $b = 12.3431(5)$, $c = 21.1918(9)$ Å, $\alpha = 88.634(3)$, $\beta = 81.852(3)°$, $\gamma = 75.398(3)$, $V = 2621.3(2)$ Å^3, $Z = 2$, $\rho = 1.478$ g cm^{-3}, μ(Mo-Kα) = 1.586 mm^{-1}, reflections: 58264 collected, 12 072 unique, $R_{int} = 0.0313$, R_1(all) = 0.0342, wR_2(all) = 0.0766.

CCDC reference numbers are 619482 (**6b**) and 619483 (**7a**), respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709551a

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