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Heteroligand copper(I) complexes of *N*-thiophosphorylated thioureas and phosphanes: Versatile structures and luminescence

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ABSTRACT

Reaction of the potassium salts of $(EtO)_2P(O)CH_2C_6H_4-4-(NHC(S)NHP(S)(OiPr)_2)$ (HL^1), $(CH_2NHC(S)NHP(S)(OiPr)_2)_2$ (H_2L^{II}) or cyclam($C(S)NHP(S)(OiPr)_2)_4$ (H_4L^{III}) with [$Cu(PPh_3)_3I$] or a mixture of CuI and Ph_2P(CH_2)_{1-3}PPh_2 or Ph_2P(C₅H_4FeC₅H_4)PPh_2 in aqueous EtOH/CH_2Cl_2 leads to [$Cu(PPh_3)L^1$] (1), [$Cu_2(Ph_2PCH_2PPh_2)_2L^{II}$] (2), [$Cu\{Ph_2P(CH_2)_2PPh_2\}L^{I}$] (3), [$Cu\{Ph_2P(CH_2)_3PPh_2\}L^{I}$] (4), [$Cu\{Ph_2P(C_5H_4FeC_5H_4)PPh_2\}L^{II}$] (7), [$Cu_2(Ph_2P(CH_2)_2PPh_2\}_2L^{II}$] (8), [$Cu_2(Ph_2P(CH_2)_3PPh_2\}_2L^{II}$] (9), [$Cu_2(Ph_2P(C_5H_4FeC_5H_4)PPh_2\}_2L^{II}$] (10), [$Cu_8(Ph_2PCH_2PPh_2)_8L^{III}I_4$] (11), [$Cu_4(Ph_2P(CH_2)_2PPh_2\}_4L^{III}$] (12), [$Cu_4(Ph_2P(CH_2)_3PPh_2\}_4L^{III}$] (13) or [$Cu_4(Ph_2P(C_5H_4FeC_5H_4)PPh_2\}_4L^{III}$] (14) complexes. The structures of these compounds were investigated by IR, ¹H, ³¹P{¹H} NMR spectroscopy; their compositions were examined by microanalysis. The luminescent properties of the complexes 1–14 in the solid state are reported.

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1. Introduction

Mono-, oligo- and polynuclear Cu(I) complexes [Cu_x(phos $phane_{v}Lig_{x}$ with neutral monodentate tertiary phosphanes PR_{3} or bidentate bis-phosphanes $R_2P-Z-PR_2$ (Z = (CH₂)_n, C₅H₄FeC₅H₄, arylene, etc.) have been extensively investigated [1]. This type of Cu(I) complexes shows an interesting structural variety and possess a number of various aggregates and associates both in solution and the solid state, and hence a number of properties (e.g. luminescent properties). The structure and electronic properties of the ligand Lig is also very important due to the fine-tuning of the structure and properties of a complex. In this connection the chalcogencontaining ligands are attractive since these donor atoms are known to adopt different coordination modes. The sulfur-containing ligands are the most widely used among them [1a,2]. This is, probably, due to the easy ways to synthesis such type of compounds compared to other chalcogen-containing ligands. A number of mixed-ligand Cu(I) complexes, containing both arylsubstituted pnictines and cyclic thioureas or pyridine thiolates, are also described [1a,2a]. Combination of these two types of ligands might lead to interesting and unusual photophysical and electrochemical properties [3].

Recently, we have described mixed-ligand Cu(I) complexes incorporating a number of *N*-thiophosphorylated thioureas or thiobenzamides, $RC(S)NHP(S)(OiPr)_2$ [4], and triphenylphosphane or

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 $Ph_2P(CH_2)_{1-3}PPh_2$ and $Ph_2P(C_5H_4FeC_5H_4)PPh_2$ phosphanes. The reaction of alkaline salts of the tetrakis-thiourea, containing a cyclam fragment cyclam(C(S)NHP(S)(OiPr)_2)_4, with [Cu(PPh_3)_3I] leads to the tetranuclear Cu(I) complex [{Cu(PPh_3)_2}_4Lig] (Chart 1) [5]. Furthermore, urea derivatives of cyclen and cyclam have, to the best of our knowledge, been reported so far in the literature by only two examples [5,6].

In this contribution we describe mixed-ligand Cu(I) complexes of $(EtO)_2P(O)CH_2C_6H_4-4-(NHC(S)NHP(S)(OiPr)_2)$ (**HL**^I), (CH₂NHC(S)-NHP(S)(OiPr)_2)_2 (**H₂L^{II}**) or cyclam(C(S)NHP(S)(OiPr)_2)_4 (**H₄L^{III}**) and phosphanes (PPh₃, Ph₂P(CH₂)₁₋₃PPh₂, Ph₂P(C₅H₄FeC₅H₄)PPh₂).

2. Results and discussion

N-Thiophosphorylated thioureas \mathbf{HL}^{I} , $\mathbf{H}_{2}\mathbf{L}^{II}$ and $\mathbf{H}_{4}\mathbf{L}^{III}$ were prepared as described previously [5,4d,7]. Reaction of the potassium salts of \mathbf{HL}^{I} , $\mathbf{H}_{2}\mathbf{L}^{I}$ or $\mathbf{H}_{4}\mathbf{L}^{III}$ with [Cu(PPh₃)₃I] or a mixture of CuI and Ph₂P(CH₂)₁₋₃PPh₂ or Ph₂P(C₅H₄FeC₅H₄)PPh₂ in aqueous EtOH/CH₂Cl₂ leads to [Cu(PPh₃)L^I] (1), [Cu₂(Ph₂PCH₂PPh₂)₂L^II] (2), [Cu{Ph₂P(CH₂)₂PPh₂}L^I] (3), [Cu{Ph₂P(CH₂)₃PPh₂}L^I] (4), [Cu{Ph₂P-(C₅H₄FeC₅H₄)PPh₂)L^{II}] (5) (Scheme 1), [Cu₂(PPh₃)₂L^{II}] (6), [Cu₂(Ph₂P(CH₂)₂PPh₂)₂L^{II}] (7), [Cu₂{Ph₂P(CH₂)₂PPh₂}₂L^{II}] (8), [Cu₂{Ph₂P(CH₂)₃PPh₂)₂L^{II}] (9), [Cu₂{Ph₂P(CF₃H₄FeC₅H₄)PPh₂}₂L^{II}] (10) (Scheme 2), [Cu₈(Ph₂PCH₂PPh₂)₈L^{III}I₄] (11), [Cu₄{Ph₂P(CH₂)₂PPh₂)₄L^{III}] (12), [Cu₄{Ph₂P(CH₂)₃PPh₂}₄L^{III}] (13) or [Cu₄{Ph₂P(C₅H₄FeC₅H₄)PPh₂}₄L^{III}] (14) (Scheme 3) complexes.

The complexes obtained are colorless crystalline powders, soluble in acetone, benzene, dichloromethane, DMSO, DMF and





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insoluble in *n*-hexane and water. ¹H, ³¹P{¹H} NMR data indicate that the deprotonated thioureas \mathbf{L}^{I-III} are coordinated through the sulfur atoms of the thiocarbonyl and thiophosphoryl groups in all the present cases studied.

It is noteworthy that the reaction of the potassium salts KL^{I} , $K_{2}L^{II}$ and $K_{4}L^{III}$ with a mixture of CuI and $Ph_{2}PCH_{2}PPh_{2}$ leads to the formation of the binuclear (2, 7) or octanuclear (11) complexes.

In our recent publications we have published the syntheses and crystal structures of similar complexes $[Cu_2(Ph_2PCH_2PPh_2){H_2 NC(S)NP(S)(OiPr)_2}]$ (15), $[Cu_2(Ph_2PCH_2PPh_2){o-C_6H_4(NHC(S) NP(S)(OiPr)_2)}]$ [4i] (16) and $[Cu_2(Ph_2PCH_2PPh_2)_2(RNHC(S)NP(S)(OiPr)_2)I]$ (R = Me, 17; Ph, 18) [4j]. Unfortunately, after numerous attempts we were not successful to get X-ray suitable crystals of the complexes. However, according to the NMR and luminescence data (see below), and elemental analyses the structure of the chelate backbones of 2, 7 and 11 are similar to the previously described complexes 15–18. The formation of 2, 7 and 11 can be explained by the rather small bite angle expected for Ph_2PCH_2Ph_2.

The IR spectrum of **HL^I** contains a band at 649 cm⁻¹ for the P=S group. It is shifted to lower wavenumbers (597–623 cm⁻¹) in the spectra of **1–5** due to the coordination with the cation. The shift is 42–52 cm⁻¹ in **1** and **3–5**, while the shift in the spectrum of **2** is 26 cm⁻¹, which might be due to the coordination of two phosphanes. The IR bands of P=S in the spectra of **6**, **8–10**, and **12–14** are shifted by 23–30 and 33–38 cm⁻¹ to lower wavenumbers relatively to the parent ligands H_2L^{II} and H_4L^{III} , respectively [5,7]. The P=S band in the IR spectra of **7** and **11** is also shifted to lower wavenumbers relatively to H_2L^{II} and H_4L^{III} ; however, the shift is 19 and 14 cm⁻¹, respectively. The appearance of the new broad and intense band at 1517–1572 cm⁻¹, due to the conjugated SCN group, also proves the formation of complexes. The presence of the substituted POC groups in **HL^I** and **1–14** can be established from the IR spectra by their absorption bands at 998–1014 cm⁻¹ [8]. Two bands for the aryINH and P(S)NH groups at 3144 and







3281 cm⁻¹ are observed in the IR spectrum of **HL**^I, whereas a unique band at 3208–3276 cm⁻¹ corresponding to the arylNH group was found in the spectra of **1–5**. It should be noted that the band of the arylNH group in the IR spectra of **1** and **2** is observed at 3208 and 3214 cm⁻¹, respectively, and in the characteristic region of amide protons participating in hydrogen bonding. The IR bands of the NH group in the spectra of **6** and **8–10** were observed at 3371–3397 cm⁻¹, shifted by 43–69 cm⁻¹ to lower wavenumbers relatively to **H₂L^{II}** (3440 cm⁻¹) [5], while the same band in the spectrum of **7** appears at 3204 cm⁻¹. The signal for the NH group is absent in the IR spectra of the complexes **11–14**.

It should be noted that in the IR spectra of **2–5** the band corresponding to the P=O fragment of the P(O)CH₂ group occurs between 1198 and 1208 cm⁻¹, that is in the same region as in the free ligand (1211 cm⁻¹). This confirms the absence of coordination of the P=O group in the P(O)CH₂ fragment of the complexes **2–5**. In the IR spectrum of **1** the absorption band of the P=O group is observed at 1158 cm⁻¹, and considerably shifted to higher frequencies compared to the spectrum of the parent ligand. This might be due to the formation of hydrogen bonds.

In the ³¹P{¹H} NMR spectra of **1–5** the resonance for the phosphoryl and thiophosphoryl groups are shown at 27.2–27.8 and 55.0–56.2 ppm, respectively [9]. The signal corresponding to the P=S group is low-field shifted, whereas the singlet for the P=O group is practically at the same region relative to those in the parent ligand **HL**¹ [4d]. In the ³¹P{¹H} NMR spectra of the complexes

6–14, the resonances in the range 50.7–57.2 ppm correspond to the phosphorus atom of the thiophosphoryl groups [9]. The signal of the phosphorus atom of PPh₃ in the spectrum of the complex **6** was found at -1.9 ppm, while the signals for the phosphane phosphorus atoms in the ³¹P{¹H} NMR spectra of the complexes **2–5** and **7–14** exhibit chemical shifts from -26.6 to -9.8 ppm.

Fast exchange between free and bound phosphane in solutions of studied complexes results in phosphane signal broadening in the ${}^{31}P{}^{1}H{}$ NMR spectra, as was observed for the Cu(I) complexes with *N*-(thio)phosphorylated thioamides and thioureas [4,5].

The ¹H NMR spectra of **2–14** contain a set of signals, corresponding to the resulting product. The spectra contain signals for the CH₃ protons at 0.81–1.76 ppm and signals for the OCH, OCH₂ and CH₂N protons at 3.19-5.33 ppm. The signals for the C₆H₄ and C₆H₅ protons in the spectra are shown as multiplets at 6.74–8.11 ppm. The $P(O)CH_2$ protons doublet signal in the spectra of 1-5 is at 3.08-3.15 ppm. The ¹H NMR spectra of 2-4, 7-9 and 11-13 contain the signals for the CH₂ protons of the corresponding phosphane Ph₂P(CH₂)₁₋₃PPh₂ and cyclam (11-13) at 1.46–4.30 ppm, while the signals for the C_5H_4 protons in the spectrum of 5, 10 and 14 are observed at 4.20-4.30 ppm. There is a singlet for the aryINH proton at 6.61-6.89 ppm in the spectra of the complexes **3–5**. The same signal in the spectrum of **2** was found at 9.85 ppm. This testifies about the hydrogen bonding in the structure of **2**. In the spectra of **6–11** the signals of the alkylNH protons were observed at 6.16–7.99 ppm and overlapped with the



Scheme 3.

signals for the Ph protons. The signal for the NHP group proton is absent in the ¹H NMR spectra of **1–14**. This confirms the presence of the ligand in the anionic form in the structure of complexes.

The luminescent properties of **1–14** were investigated in the solid state at room temperature. The data are listed in Table 1. From the emission behavior we can define four different groups of complexes. First, the two complexes **1** and **6**, which show no emission in the solid state. Second, the complexes **3–5**, **8–10** and **12–14**. Their emission maxima vary only slightly between 466 and 487 nm. The complex **7**, which contains Ph₂PCH₂PPh₂ as a chelate phosphane ligand, forms the third group and shows emission at 519 nm. The last group is formed by the two complexes **2** and **11**, which also contain Ph₂PCH₂PPh₂ as a chelate phosphane ligand, and the iodine ligand, which is bound to one of the copper atoms (Schemes 1 and 3). It is noteworthy that neither the parent ligands

 Table 1

 Photophysical data for 1–14.

Complex	Emission maximum (nm)
1	No emission
2	448, 618
3	466
4	470
5	487
6	No emission
7	519
8	478
9	469
10	482
11	452, 614
12	461
13	463
14	486

 HL^{I} , $H_{2}L^{II}$ and $H_{4}L^{III}$, nor their corresponding potassium salts show emission in the solid state at the same experimental conditions.

Emissions around 450-510 nm are typical of Cu-phosphane containing chromophores with either ILCT (σ - a_{π}) or MLCT (d- σ^*) excited states [10]. Therefore, we can assign the emission (³ILCT or ³MLCT) from the observed energies and the marked dependence on the type of the phosphane ligand (see last three groups), although a ${}^{3}\pi$ - π^{*} contribution of the thiourea ligand anions (L^{I-III}) cannot be ruled out completely. The differences in the emission spectra probably arise from the fact that while PPh₃ can only provide one type of σ - a_{π} transition, the chelate phosphane ligands additionally contain bridging alkyl or ferrocenyl groups. The propensity to emit (or not) very probably depend on the geometry of the Cu-phosphane chromophore, which is largely depending on the chelate bite angle of the ligand. One interesting point in this respect is the unusual emission for the complex 7, which might be due to contributions from cluster-centered charge transfer transition in this binuclear aggregate, probably containing rather short Cu1...Cu2 distances, similar to 15 and 16 [4i]. Furthermore, the emission spectra of the complexes 2 and 11, besides the blue emission band, which is in the same area as in the spectra of the complexes 3-5, 8-10 and 12-14, contain the low energy band (Table 1). On the basis of these experiments we can draw the conclusion that the presence of the iodine ligands in 2 and 11 are connected to the observation of the long-wavelength emissions around 615 nm. Presumably they originate from ligand (I⁻) to metal (Cu(I)) charge transfer transition, similar to 17 and 18 [4j].

3. Experimental

All chemicals and reagents were purchased from commercial sources and used as received. All syntheses were carried out under ambient conditions. *N*-Thiophosphorylthiourea \mathbf{HL}^{II} , \mathbf{H}_{2L}^{III} and \mathbf{H}_{4L}^{III} and the complex **1** were prepared as previously described [5,4d,7].

HL^I: IR v(cm⁻¹): 649 (P=S), 1009 (POC), 1211 (P=O), 1569 (S=C-N), 3144, 3281 (NH).

1: mp 127–128 °C (127 °C [4d]). IR v(cm⁻¹): 597 (P=S), 998 (POC), 1158 (P=O), 1544 (SCN), 3208 (NH).

3.1. Synthesis of 2-5

A suspension of **HL**¹ (0.241 g, 0.5 mmol) in aqueous ethanol (35 mL) was mixed with an ethanol solution of potassium hydroxide (0.031 g, 0.55 mmol). A mixture of Cul (0.095 g, 0.5 mmol) and Ph₂P(CH₂)_nPPh₂ (n = 1, 0.192 g; n = 2, 0.199 g; n = 3, 0.206 g; 0.5 mmol) or Ph₂P(C₅H₄FeC₅H₄)PPh₂ (0.277 g, 0.5 mmol) in CH₂Cl₂ (25 mL) was refluxed for 0.5 h and then added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred for an hour and the precipitate was filtered off. The filtrate was concentrated until crystallization began. Isolated crystals were obtained from a CH₂Cl₂/n-hexane mixture 1:5 (v/v).

2: Yield 0.275 g (73%), mp 204–205 °C. IR $v(\text{cm}^{-1})$: 623 (P=S), 1014 (POC), 1207 (P=O), 1567 (SCN), 3214 (NH). ¹H NMR (DMSO-*d*₆) δ (ppm): 1.07–1.34 (m, 18H, CH₃, EtO + *i*PrO), 2.48 (br. s, 4H, CH₂), 3.12 (d, ²*J*_{P,H} = 21.3 Hz, 2H, CH₂, P(O)CH₂), 3.88–4.06 (m, 4H, OCH₂, EtO), 4.62 (d. sept, ³*J*_{H,H} = 6.1 Hz, ³*J*_{POCH} = 10.0 Hz, 2H, OCH, *i*PrO), 7.07–7.84 (m, overlapping with the solvent signal, C₆H₄ + C₆H₅), 9.85 (s, 1H, NH); ³¹P{¹H} NMR (DMSO-*d*₆) δ (ppm): –24.6 to –13.8 (m, 4P, PPh₂), 27.8 (s, 1P, P=O), 56.2 (s, 1P, P=S). *Anal.* Calc. for C₆₈H₇₅Cu₂IN₂O₅P₆S₂ (1504.31): C, 54.29; H, 5.03; N, 1.86. Found: C, 54.13; H, 5.09; N, 1.82%.

3: Yield 0.382 g (81%), mp 83–84 °C. IR $v(\text{cm}^{-1})$: 602 (P=S), 1001 (POC), 1203 (P=O), 1553 (SCN), 3274 (NH). ¹H NMR (CDCl₃) δ (ppm): 1.12–1.33 (m, 18H, CH₃, EtO + *i*PrO), 2.30 (br. s, 4H, CH₂), 3.08 (d, ²*J*_{P,H} = 20.8 Hz, 2H, CH₂, P(O)CH₂), 3.81–3.99 (m, 4H, OCH₂, EtO), 4.75 (d. sept, ³*J*_{H,H} = 6.2 Hz, ³*J*_{POCH} = 9.7 Hz, 2H, OCH, *i*PrO), 6.72 (s, 1H, NH), 7.16–7.96 (m, overlapping with the solvent signal, C₆H₄ + C₆H₅); ³¹P{¹H} NMR (CDCl₃) δ (ppm): –12.8 (br. s, 2P, PPh₂), 27.3 (s, 1P, P=O), 55.3 (1P, P = S). *Anal.* Calc. for C₄₄H₅₅Cu-N₂O₅P₄S₂ (943.49): C, 56.01; H, 5.88; N, 2.97. Found: C, 56.15; H, 5.93; N, 2.90%.

4: Yield 0.455 g (95%), mp 70–71 °C. IR $v(cm^{-1})$: 599 (P=S), 1007 (POC), 1208 (P=O), 1548 (SCN), 3269 (NH). ¹H NMR (CDCl₃) δ (ppm): 1.03–1.27 (m, 18H, CH₃, EtO + *i*PrO), 2.38 (br. s, 4H, CH₂), 2.85 (br. s, 2H, CH₂), 3.13 (d, ²*J*_{P,H} = 20.4 Hz, 2H, CH₂, P(O)CH₂), 3.91–4.08 (m, 4H, OCH₂, EtO), 4.54 (d. sept, ³*J*_{H,H} = 6.0 Hz, ³*J*_{POCH} = 10.3 Hz, 2H, OCH, *i*PrO), 6.61 (s, 1H, NH), 7.03–7.71 (m, overlapping with the solvent signal, C₆H₄ + C₆H₅); ³¹P{¹H} NMR (CDCl₃) δ (ppm): –16.4 (br. s, 2P, PPh₂), 27.6 (s, 1P, P=O), 55.0 (s, 1P, P=S). *Anal.* Calc. for C₄₅H₅₇CuN₂O₅P₄S₂ (957.52): C, 56.45; H, 6.00; N, 2.93. Found: C, 56.38; H, 6.08; N, 2.90%.

5: Yield 0.434 g (79%), mp 93–94 °C. IR $v(\text{cm}^{-1})$: 607 (P=S), 1011 (POC), 1198 (P=O), 1558 (SCN), 3276 (NH). ¹H NMR (CDCl₃) δ (ppm): 0.98–1.22 (m, 18H, CH₃, EtO + *i*PrO), 3.15 (d, ²J_{P,H} = 20.9 Hz, 2H, CH₂, P(O)CH₂), 3.77–4.06 (m, 4H, OCH₂, EtO), 4.24 (br. s, 4H, C₅H₄), 4.29 (br. s, 4H, C₅H₄), 4.62 (d. sept, ³J_{H,H} = 6.1 Hz, ³J_{POCH} = 9.3 Hz, 2H, OCH, *i*PrO), 6.89 (s, 1H, NH), 7.23–8.11 (m, overlapping with the solvent signal, C₆H₄ + C₆H₅); ³¹P{¹H</sup> NMR (CDCl₃) δ (ppm): -16.9 (br. s, 2P, PPh₂), 27.2 (s, 1P, P=O), 54.8 (s, 1P, P=S). *Anal.* Calc. for C₅₂H₅₉CuFeN₂O₅P₄S₂ (1099.46): C, 56.81; H, 5.41; N, 2.55. Found: C, 56.92; H, 5.36; N, 2.51%.

3.2. Synthesis of 6

A suspension of H_2L^{II} (0.269 g, 0.5 mmol) in ethanol (35 mL) was mixed with an ethanol solution of potassium hydroxide

(0.062 g, 1.1 mmol). A solution of $[Cu(PPh_3)_3I]$ (0.977 g, 1.0 mmol) in CH₂Cl₂ (25 mL) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred for an hour and the resulting precipitate of KI was filtered off. The filtrate was concentrated until crystallization began. Isolated crystals were precipitated from a dichloromethane/*n*-hexane mixture 1:5 (v/v).

6: Yield 0.702 g (82%), mp 109–110 °C. IR $v(\text{cm}^{-1})$: 610 (P=S), 1001 (POC), 1529 (SCN), 3371 (NH). ¹H NMR (CDCl₃) δ (ppm): 1.27 (d, ³*J*_{H,H} = 6.0 Hz, 12H, CH₃, *i*Pr), 1.30 (d, ³*J*_{H,H} = 6.1 Hz, 12H, CH₃, *i*Pr), 3.48 (br. s, 4H, CH₂N), 4.73 (d. sept, ³*J*_{H,H} = 6.0 Hz, ³*J*_{P,H} = 10.9 Hz, 4H, OCH), 6.16 (br. s, 2H, NH), 7.28–7.46 (m, 60H, Ph); ³¹P{¹H} NMR (CDCl₃) δ (ppm): –1.9 (s, 4P, PPh₃), 54.6 (s, 2P, NPS). *Anal.* Calc. for C₈₈H₉₄Cu₂N₄O₄P₆S₄ (1712.91): C, 61.71; H, 5.53; N, 3.27. Found: C, 61.83; H, 5.46; N, 3.21%.

3.3. Synthesis of 7-10

A suspension of H_2L^{II} (0.269 g, 0.5 mmol) in 96 % aqueous ethanol (35 mL) was mixed with an 96% ethanol solution of potassium hydroxide (0.062 g, 1.1 mmol). A mixture of CuI (0.19 g, 1.0 mmol) and Ph₂P(CH₂)_nPPh₂ (n = 1, 0.384 g; n = 2, 0.398 g; n = 3, 0.412 g; 1.0 mmol) or Ph₂P(C₅H₄FeC₅H₄)PPh₂ (0.554 g, 1.0 mmol) in CH₂Cl₂ (25 mL) was refluxed for 0.5 h and then added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred for an hour and the precipitate of KI was filtered off. The filtrate was concentrated until crystallization began. Isolated solid materials were obtained from a dichloromethane/*n*-hexane mixture 1:3 (v/v).

7: Yield 0.388 g (74%), mp 58–59 °C. IR $v(\text{cm}^{-1})$: 621 (P=S), 1004 (POC), 1572 (SCN), 3204 (NH). ¹H NMR (CDCl₃) δ (ppm): 1.04–1.76 (m, 24H, CH₃, *i*Pr), 2.91 (br. s, 2H, CH₂), 4.30–5.33 (m, 8H, OCH + CH₂N), 6.79–7.59 (m, overlapped with the solvent signal, NH + Ph); ³¹P{¹H} NMR (CDCl₃) δ (ppm): –9.8 (s, 2P, PPh₂), 57.2 (s, 2P, NPS). *Anal.* Calc. for C₄₁H₅₆Cu₂N₄O₄P₄S₄ (1048.15): C, 46.98; H, 5.39; N, 5.35. Found: C, 47.13; H, 5.28; N, 5.41%.

8: Yield 0.635 g (87%), mp 83–84 °C. IR $v(cm^{-1})$: 611 (P=S), 1014 (POC), 1522 (SCN), 3386 (NH). ¹H NMR (CDCl₃) δ (ppm): 1.28 (br. s, 24H, CH₃, *i*Pr), 2.27 (br. s, 8H, CH₂), 3.47 (br. s, 4H, CH₂N), 4.69 (br. s, 4H, OCH), 6.82–7.99 (m, overlapped with the solvent signal, NH + Ph); ³¹P{¹H} NMR (CDCl₃) δ (ppm): –12.5 (br. s, 4P, PPh₂), 53.7 (s, 2P, NPS). *Anal.* Calc. for C₆₈H₈₂Cu₂N₄O₄P₆S₄ (1460.60): C, 55.92; H, 5.66; N, 3.84. Found: C, 55.79; H, 5.73; N, 3.80%.

9: Yield 0.588 g (79%), mp 67–68 °C. IR $v(\text{cm}^{-1})$: 617 (P=S), 1009 (POC), 1534 (SCN), 3397 (NH). ¹H NMR (CDCl₃) δ (ppm): 1.03–1.35 (m, 24H, CH₃, iPr), 1.74 (br. s, 4H, CH₂), 2.34 (br. s, 8H, CH₂), 3.28 (br. s, 4H, CH₂N), 4.68 (br. s, 4H, OCH), 6.83–7.71 (m, overlapped with the solvent signal, NH + Ph); ³¹P{¹H} NMR (CDCl₃) δ (ppm): –19.6 (br. s, 4P, PPh₂), 56.0 (s, 2P, NPS). *Anal.* Calc. for C₇₀H₈₆Cu₂N₄O₄P₆S₄ (1488.65): C, 56.48; H, 5.82; N, 3.76. Found: C, 56.32; H, 5.75; N, 3.80%.

10: Yield 0.610 g (68%), mp 142–143 °C. IR $v(\text{cm}^{-1})$: 614 (P=S), 1012 (POC), 1527 (SCN), 3373 (NH). ¹H NMR (CDCl₃) δ (ppm): 0.81–0.93 (m, 24H, CH₃, *i*Pr), 3.19 (br. s, 4H, CH₂N), 4.21 (br. s, 8H, C₅H₄), 4.29 (br. s, 8H, C₅H₄), 4.46–4.91 (m, 8H, OCH + CH₂N), 7.16–7.48 (m, overlapped with the solvent signal, NH + Ph); ³¹P{¹H} NMR (CDCl₃) δ (ppm): –17.9 (br. s, 4P, PPh₂), 56.2 (s, 2P, NPS). *Anal.* Calc. for C₈₄H₉₀Cu₂Fe₂N₄O₄P₆S₄ (1772.53): C, 56.92; H, 5.12; N, 3.16. Found: C, 56.81; H, 5.18; N, 3.22%.

3.4. Synthesis of 11-14

A suspension of **H₄L^{III}** (0.116 g, 0.1 mmol) in 96% aqueous ethanol (10 mL) was mixed with an 96% ethanol solution of potassium hydroxide (0.025 g, 0.44 mmol). A mixture of CuI (0.076 g, 0.4 mmol) and Ph₂P(CH₂)_nPPh₂ (n = 1, 0.154 g; n = 2, 0.159 g;

n = 3, 0.165 g; 0.4 mmol) or Ph₂P(C₅H₄FeC₅H₄)PPh₂ (0.222 g, 0.4 mmol) in CH₂Cl₂ (10 mL) was refluxed for 5 min and then added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred for an hour and the resulting precipitate of KI was filtered off. The filtrate was concentrated until crystallization began. Isolated solid materials were obtained from a dichloromethane/*n*-hexane mixture 1:5 (v/v).

11: Yield 0.186 g (71%), mp 193–194 °C. IR v(cm⁻¹): 642 (P=S), 1013 (POC), 1558 (SCN). ¹H NMR (DMSO- d_6) δ (ppm): 1.31 (d, ${}^{3}J_{H,H}$ = 6.0 Hz, 48 H, CH₃, *i*Pr), 1.52–4.48 (m, 36 H, CH₂), 4.76 (d. sept, ${}^{3}J_{H,H} = 6.2 \text{ Hz}, {}^{3}J_{P,H} = 9.7 \text{ Hz}, 8 \text{ H}, \text{ OCH}), 6.74-8.11 (m, 160 \text{ H}, \text{ Ph});$ $^{31}P{^{1}H}$ NMR (DMSO- d_6) δ (ppm): -26.9 to -11.4 (m, 16 P, PPh₂), 51.4 (s, 4 P, NPS). Anal. Calc. for C₂₃₈H₂₅₆Cu₈I₄N₈O₈P₂₀S₈ (5248.64): C, 54.46; H, 4.92; N, 2.13. Found: C, 54.68; H, 5.03; N, 2.07%.

12: Yield 0.252 g (84%), mp 96–97 °C. IR $v(cm^{-1})$: 623 (P=S), 1008 (POC), 1517 (SCN). ¹H NMR (CDCl₃) δ (ppm): 1.17–1.29 (m, 48 H, CH₃, *i*Pr), 1.46-4.31 (m, 36 H, CH₂), 4.84 (d. sept, ${}^{3}I_{HH} = 6.1 \text{ Hz}, {}^{3}I_{PH} = 10.2 \text{ Hz}, 8 \text{ H}, \text{ OCH}), 6.91-7.72 (m, overlapped)$ with the solvent signal, Ph); ${}^{31}P{}^{1}H$ NMR (CDCl₃) δ (ppm): -13.8 (br. s, 8 P, PPh₂), 50.7 (s, 4 P, NPS). Anal. Calc. for C₁₄₂H₁₇₂Cu₄-N₈O₈P₁₂S₈ (3001.33): C, 56.83; H, 5.78; N, 3.73. Found: C, 56.68; H. 5.82: N. 3.68%.

13: Yield 0.223 g (73%), mp 118–119 °C. IR v(cm⁻¹): 620 (P=S), 1012 (POC), 1528 (SCN). ¹H NMR (CDCl₃) δ (ppm) 1.22 (d, ${}^{3}J_{\rm H,H}$ = 6.0 Hz, 24 H, CH₃, iPr), 1.29 (d, ${}^{3}J_{\rm H,H}$ = 6.2 Hz, 24 H, CH₃, iPr), 1.50–4.53 (m, 44 H, CH₂), 4.69 (d. sept, ${}^{3}J_{\rm H,H}$ = 6.0 Hz, ${}^{3}J_{\rm P,H}$ = 10.1 Hz, 8 H, OCH), 7.14-8.06 (m, overlapped with the solvent signal, Ph); ³¹P{¹H} NMR (CDCl₃) δ (ppm): -17.1 (br. s, 8 P, PPh₂), 50.9 (s, 4 P, NPS). Anal. Calc. for C₁₄₆H₁₈₀Cu₄N₈O₈P₁₂S₈ (3057.43): C, 57.36; H, 5.93; N, 3.66. Found: C, 57.42; H, 5.98; N, 3.74%.

14: Yield 0.334 g (92%), mp 153–154 °C. IR v(cm⁻¹): 618 (P=S), 1004 (POC), 1524 (SCN). ¹H NMR (CDCl₃) δ (ppm): 1.08–1.34 (m, 48 H, CH₃, *i*Pr), 1.67–4.59 (m, 42 H, CH₂ + C₅H₄), 4.69 (d. sept, ${}^{3}J_{H,H}$ = 6.1 Hz, ${}^{3}J_{P,H}$ = 10.9 Hz, 8 H, OCH), 7.19–7.94 (m, overlapped with the solvent signal, Ph); ${}^{31}P{}^{1}H$ NMR (CDCl₃) δ (ppm): -20.7 (br. s, 8 P, PPh₂), 51.1 (s, 4 P, NPS). Anal. Calc. for C₁₇₄H₁₈₈Cu₄Fe₄-N₈O₈P₁₂S₈ (3625.19): C, 57.65; H, 5.23; N, 3.09. Found: C, 57.41; H. 5.27: N. 3.14%.

3.5. Physical measurements

Infrared spectra (Nujol) were recorded with a Bruker IFS66vS 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 were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and 85% H₃PO₄ (³¹P{¹H}). Fluorescence measurements were carried out on a FL 3-221-NIR Jobin Jvon spectrofluorometer at room temperature. Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer.

4. Conclusions

In summary, the reaction of [Cu(PPh₃)₃I] or a mixture of CuI and $Ph_2P(CH_2)_{1-3}PPh_2$ or $Ph_2P(C_5H_4FeC_5H_4)PPh_2$ with the potassium salts of HL^I, H₂L^{II} or H₄L^{III} has allowed us to obtain complexes 1-14. The formation of the complexes 2, 7 and 11 is favored by the small bite angle of the Ph₂PCH₂PPh₂ diphosphane. The complex **1** forms dimers in the crystal by the NH function and the oxygen atom of the phosphoryl P=O group.

The complexes 2–5 and 7–14 exhibit emission in the solid state at ambient temperature. Furthermore, the complexes 2 and 11 exhibits marked long-wavelength emission in the solid state under the same conditions.

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