

Note

Copper(I) Complexes of *N*-thiophosphorylated Bis-thiourea [CH₂NHC(S)NHP(S)(*OiPr*)₂]₂ and Phosphines (PPh₃, Ph₂P(CH₂)_{1–3}PPh₂, Ph₂P(C₅H₄FeC₅H₄)PPh₂): Versatile Structures and Luminescence

Damir A. Safin,* Maria G. Babashkina, and Axel Klein

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

RECEIVED OCTOBER 09, 2010; REVISED FEBRUARY 16, 2010; ACCEPTED FEBRUARY 17, 2010

Abstract. Reaction of the potassium solution of [CH₂NHC(S)NHP(S)(*OiPr*)₂]₂ (**H₂L**) with [Cu(PPh₃)₃] or a mixture of CuI and Ph₂P(CH₂)_{1–3}PPh₂ or Ph₂P(C₅H₄FeC₅H₄)PPh₂ in aqueous EtOH/CH₂Cl₂ leads to binuclear [Cu₂(PPh₃)₂L] (**1**), [Cu₂(Ph₂PCH₂PPh₂)L] (**2**), [Cu₂{Ph₂P(CH₂)₂PPh₂}₂L] (**3**), [Cu₂{Ph₂P(CH₂)₃PPh₂}₂L] (**4**) or [Cu₂{Ph₂P(C₅H₄FeC₅H₄)PPh₂}₂L] (**5**) complexes. The structures of these compounds were investigated by IR, ¹H and ³¹P{¹H} NMR spectroscopy; their compositions were examined by microanalysis. The luminescent properties of complexes **1–5** in the solid state are reported.

Keywords: coordination chemistry, copper(I), thiophosphorylthiourea, phosphine, luminescence

INTRODUCTION

In our preceding papers, we have described the heteroligand Cu(I) complexes with a number of *N*-thiophosphorylated thioureas and thioamide RC(S)NHP(S)(*OiPr*)₂ (R = morpholin-*N*-yl, piperidin-*N*-yl;¹ *α*-naphthylNH;² NH₂;^{1,3,4} pyridin-2-ylNH, pyridin-3-ylNH, H₂N-6-Py-2-NH;⁵ Ph, Et₂N;^{6–8} (EtO)₂-P(O)CH₂C₆H₄-4-NH;⁹ MeNH, *i*PrNH, *t*BuNH, Me₂N, PhNH, 2,6-Me₂C₆H₃NH, 2,4,6-Me₃C₆H₂NH^{10,11}), and triphenylphosphine or Ph₂P(CH₂)_{1–3}PPh₂ and Ph₂P(C₅H₄FeC₅H₄)PPh₂ phosphines. Furthermore, the reaction of alkaline salts of the tetrakis-thiourea, containing a cyclam fragment cyclam[C(S)NHP(S)(*OiPr*)₂]₄ (**H₄Q**), with [Cu(PPh₃)₃] leads to the tetranuclear Cu(I) complex [Cu(PPh₃)₂]₄Q.¹²

On the other hand we have described a number of *N*-(thio)phosphorylated bis-(thio)ureas and their complexation properties towards various metal cations.^{7,13–21} Only one heteroligand Cu^I complex with *N*-thiophosphoryl bis-thiourea, containing 1,10-diaza-18-crown-6, and PPh₃ have been described.⁷ To the best of our knowledge, there are no crystal structures of such type of complexes.

In this contribution we describe binuclear heteroligand Cu(I) complexes of [CH₂NHC(S)NHP(S)(*OiPr*)₂]₂ (**H₂L**) and phosphines (PPh₃, Ph₂P(CH₂)_{1–3}PPh₂, Ph₂P(C₅H₄FeC₅H₄)PPh₂) with the purpose of the structure characterization and luminescent properties investigation.

EXPERIMENTAL

Physical measurements

Infrared spectra were recorded with a Bruker IFS66vS 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}). Fluorescence measurements were carried out on a Spex FluoroMax-3 spectrofluorometer at room temperature. Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer.

N-Thiophosphorylated thiourea **H₂L** was prepared according to the previously described method.¹⁴

Synthesis of 1

A suspension of **H₂L** (0.269 g, 0.5 mmol) in 96 % aqueous ethanol (35 mL) was mixed with a 96 % ethanol solution of potassium hydroxide (0.062 g, 1.1 mmol). A solution of [Cu(PPh₃)₃] (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 crystallisation began. Isolated crystals were precipitated from a dichloro-methane/*n*-hexane mixture (*φ* = 0.17).

* Author to whom correspondence should be addressed. (E-mail: damir.safin@ksu.ru)

Yield: 0.702 g (82 %); ^1H NMR δ/ppm : 1.27 (d, $^3J_{\text{H,H}} = 6.0$ Hz, 12H, CH_3 , *i*Pr), 1.30 (d, $^3J_{\text{H,H}} = 6.1$ Hz, 12H, CH_3 , *i*Pr), 3.48 (br. s, 4H, CH_2N), 4.73 (d. sept, $^3J_{\text{H,H}} = 6.0$ Hz, $^3J_{\text{P,H}} = 10.9$ Hz, 4H, OCH), 6.16 (br. s, 2H, NH), 7.28–7.46 (m, 60H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR δ/ppm : -1.9 (s, 4P, PPh_3), 54.6 (s, 2P, NPS); IR $\nu_{\text{max}}/\text{cm}^{-1}$: 610 (P=S), 1001 (POC), 1529 (SCN), 3371 (NH).

Anal. Calcd. mass fractions of elements, w/%, for $\text{C}_{88}\text{H}_{94}\text{Cu}_2\text{N}_4\text{O}_4\text{P}_6\text{S}_4$ ($M_r = 1712.91$) are: C 61.71, H 5.53, N 3.27; found: C 61.83, H 5.46, N 3.21.

Synthesis of 2–5

A suspension of H_2L (0.269 g, 0.5 mmol) in 96 % aqueous ethanol (35 mL) was mixed with a 96 % ethanol solution of potassium hydroxide (0.062 g, 1.1 mmol). A mixture of CuI (0.19 g, 1.0 mmol) and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$, 0.384 g; $n = 2$, 0.398 g; $n = 3$, 0.412 g; 1.0 mmol) or $\text{Ph}_2\text{P}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4)\text{PPh}_2$ (0.554 g, 1.0 mmol) in CH_2Cl_2 (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 ($\varphi = 0.25$).

2. Yield: 0.388 g (74 %); ^1H NMR δ/ppm : 1.04–1.76 (m, 24H, CH_3 , *i*Pr), 2.91 (br. s, 2H, CH_2), 4.30–5.33 (m, 8H, OCH + CH_2N), 6.79–7.59 (m, overlapped with the solvent signal, NH + Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR δ/ppm : -9.8 (s, 2P, PPh_2), 57.2 (s, 2P, NPS); IR $\nu_{\text{max}}/\text{cm}^{-1}$: 621 (P=S), 1004 (POC), 1572 (SCN), 3204 (NH).

Anal. Calcd. mass fractions of elements, w/%, for $\text{C}_{41}\text{H}_{56}\text{Cu}_2\text{N}_4\text{O}_4\text{P}_4\text{S}_4$ ($M_r = 1048.15$) are: C 46.98, H 5.39, N 5.35; found: C 47.13, H 5.28, N 5.41.

3. Yield: 0.635 g (87 %); ^1H NMR δ/ppm : 1.28 (br. s, 24H, CH_3 , *i*Pr), 2.27 (br. s, 8H, CH_2), 3.47 (br. s, 4H, CH_2N), 4.69 (br. s, 4H, OCH), 6.82–7.99 (m, overlapped with the solvent signal, NH + Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR δ/ppm : -12.5 (br. s, 4P, PPh_2), 53.7 (s, 2P, NPS); IR $\nu_{\text{max}}/\text{cm}^{-1}$: 611 (P=S), 1014 (POC), 1522 (SCN), 3386 (NH).

Anal. Calcd. mass fractions of elements, w/%, for $\text{C}_{68}\text{H}_{82}\text{Cu}_2\text{N}_4\text{O}_4\text{P}_6\text{S}_4$ ($M_r = 1460.60$): C 55.92, H 5.66, N 3.84; found: C 55.79, H 5.73, N 3.80.

4. Yield: 0.588 g (79 %); ^1H NMR δ/ppm : 1.03–1.35 (m, 24H, CH_3 , *i*Pr), 1.74 (br. s, 4H, CH_2), 2.34 (br. s, 8H, CH_2), 3.28 (br. s, 4H, CH_2N), 4.68 (br. s, 4H, OCH), 6.83–7.71 (m, overlapped with the solvent signal, NH + Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR δ/ppm : -19.6 (br. s, 4P, PPh_2), 56.0 (s, 2P, NPS); IR $\nu_{\text{max}}/\text{cm}^{-1}$: 617 (P=S), 1009 (POC), 1534 (SCN), 3397 (NH).

Anal. Calcd. mass fractions of elements, w/%, for $\text{C}_{70}\text{H}_{86}\text{Cu}_2\text{N}_4\text{O}_4\text{P}_6\text{S}_4$ ($M_r = 1488.65$): C 56.48, H 5.82, N 3.76; found: C 56.32, H 5.75, N 3.80.

5. Yield: 0.610 g (68 %); ^1H NMR δ/ppm : 0.81–0.93 (m, 24H, CH_3 , *i*Pr), 3.19 (br. s, 4H, CH_2N), 4.21 (br. s, 8H, C_5H_4), 4.29 (br. s, 8H, C_5H_4), 4.46–4.91 (m, 8H, OCH + CH_2N), 7.16–7.48 (m, overlapped with the solvent signal, NH + Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR δ/ppm : -17.9 (br. s, 4P, PPh_2), 56.2 (s, 2P, NPS); IR $\nu_{\text{max}}/\text{cm}^{-1}$: 614 (P=S), 1012 (POC), 1527 (SCN), 3373 (NH).

Anal. Calcd. mass fractions of elements, w/%, for $\text{C}_{84}\text{H}_{90}\text{Cu}_2\text{Fe}_2\text{N}_4\text{O}_4\text{P}_6\text{S}_4$ ($M_r = 1772.53$): C 56.92, H 5.12, N 3.16; found: C 56.81, H 5.18, N 3.22.

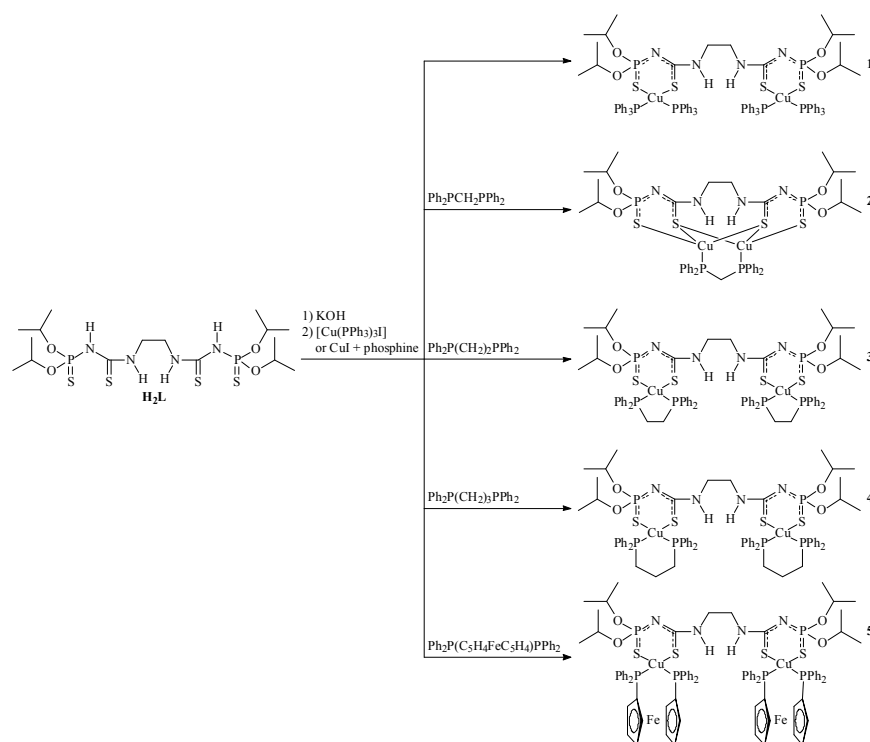
RESULTS AND DISCUSSION

N-Thiophosphorylated thiourea H_2L was prepared as described previously.¹⁴ Reaction of the potassium solution of H_2L with $[\text{Cu}(\text{PPh}_3)_3\text{I}]$ or a mixture of CuI and $\text{Ph}_2\text{P}(\text{CH}_2)_{1-3}\text{PPh}_2$ or $\text{Ph}_2\text{P}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4)\text{PPh}_2$ in aqueous EtOH/ CH_2Cl_2 leads to binuclear $[\text{Cu}_2(\text{PPh}_3)_2\text{L}]$ (**1**), $[\text{Cu}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{L}]$ (**2**), $[\text{Cu}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}_2\text{L}]$ (**3**), $[\text{Cu}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}_2\text{L}]$ (**4**) or $[\text{Cu}_2\{\text{Ph}_2\text{P}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4)\text{PPh}_2\}_2\text{L}]$ (**5**) complexes (Scheme 1).

The complexes obtained are colorless crystalline powders, soluble in acetone, benzene, dichloromethane, DMSO, DMF and insoluble in *n*-hexane. ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR and IR data indicated that the deprotonated thiourea **L** is coordinated through the sulfur atoms of the thiocarbonyl and thiophosphoryl groups in all the present cases studied.

The IR bands of P=S in the spectra of **1** and **3–5** are shifted by 23–30 cm^{-1} to lower wavenumbers relatively to the parent ligands H_2L .¹⁴ This confirms the chelate formation with the metal ion. The P=S band in the IR spectrum of **2** is also shifted to lower wavenumbers relatively to H_2L ; however, the shift is 19 cm^{-1} . The intensive absorption band of the conjugated thioamide group in the spectra of **1** and **3–5** is observed at 1522–1534 cm^{-1} , while the same band in the IR spectrum of **2** is shown at 1572 cm^{-1} . Presence of a wide absorption band of the POC fragments in **1–5** in the area 1001–1014 cm^{-1} confirms the presence of the substituted phosphoric fragment. The IR bands of the ethyleneNH group in the spectra of **1** and **3–5** were observed at 3371–3397 cm^{-1} and 43–69 cm^{-1} shifted to lower wavenumbers relatively to H_2L (3440 cm^{-1}),¹⁴ while the same band in the spectrum of **2** was shown at 3204 cm^{-1} .

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the complexes, the resonances in the range 54.6–57.2 ppm correspond to the phosphorus atom of the thiophosphoryl group. These signals are low-field shifted relative to that in the spectrum of H_2L ($\delta = 51.5$ ppm¹⁴). The signal of the phosphorus atom of PPh_3 in the spectrum of the complex **1** was found at -1.9 ppm, while the signals for the phosphine phosphorus atoms in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the complexes **2–5** exhibit chemical shifts from -19.6 to -9.8 ppm.



Scheme 1. Formation of Cu(I) complexes.

The ^1H NMR spectra of **1–5** contain only signals which correspond to the proposed structures. The spectra contain signals for the CH_3 protons at 0.81–1.76 ppm and signals for the OCH and CH_2N protons at 3.19–5.33 ppm. The signal for the ethyleneNH protons in the spectra of **1–5** were observed at 6.16–7.99 ppm and overlapped with the signals for the Ph protons. The signal for the NHP group proton is absent in the ^1H NMR spectra of **1–5**. This confirms the presence of the ligand anionic form in the structure of complexes. The ^1H NMR spectra of **2–4** contain the signals for the CH_2 protons of the phosphines $\text{Ph}_2\text{P}(\text{CH}_2)_{1-3}\text{PPh}_2$ at 1.74–2.91 ppm, while the signals for the C_5H_4 protons in the spectrum of **5** are observed at 4.21–4.29 ppm.

It is noteworthy that the reaction of the potassium solution of **H₂L** with a mixture of CuI and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ leads to the formation of the binuclear complex **2**. In our recent publications we have published the synthesis and crystal structure of the similar complexes $[\text{Cu}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\{\text{H}_2\text{NC}(\text{S})\text{NP}(\text{S})(\text{O}i\text{Pr})_2\}_2]$ (**6**) and $[\text{Cu}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\{o\text{-C}_6\text{H}_4[\text{NHC}(\text{S})\text{NP}(\text{S})$

$(\text{O}i\text{Pr})_2\}_2]$ (**7**).²² 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** are similar to the previously described complexes **6** and **7**. The formation of **2** can be explained by the rather small bite angle expected for $\text{Ph}_2\text{PCH}_2\text{PPh}_2$.

The luminescent properties of **1–5** were investigated in the solid state at room temperature. It was found that the complex **1** shows no emission. The complexes **3–5** show blue emission band with the maximum intensity at 469–484 nm (Table 1). The complex **2** shows emission at 519 nm (Table 1).

The emission around 450–510 nm is typical of Cu–P containing chromophores.^{23,24} Thus, the excited state responsible for the luminescence of the monomeric species can be assigned to a metal-to-ligand charge transfer of the type $\text{Cu}(\text{I}) \rightarrow \pi^*(\text{PPh}_2)$. The low-energy and stronger emission for the complex **2** seems to be originate from mainly a metal-to-ligand charge transfer of the type $\text{Cu}(\text{I}) \rightarrow \pi^*(\text{PPh}_2)$ mixed with a cluster-centred charge transfer transition due to the binuclear aggregate.^{4,8,11,22}

Table 1. Photophysical data for complexes **1–5**

Complex	Emission maximum (nm)
1	/
2	519
3	478
4	469
5	484

CONCLUSION

Reaction of $[\text{Cu}(\text{PPh}_3)_3]\text{I}$ or a mixture of CuI and $\text{Ph}_2\text{P}(\text{CH}_2)_{1-3}\text{PPh}_2$ or $\text{Ph}_2\text{P}(\text{C}_5\text{H}_4\text{FeC}_3\text{H}_4)\text{PPh}_2$ with the potassium solution of the *N*-thiophosphorylated bis-

thiourea **H₂L** has allowed us to obtain binuclear complexes **1–5**.

The formation of the binuclear complex **2** is favored by the small bite angle of the Ph₂PCH₂PPh₂ diphosphine combined with a small steric demand of the ethylene spacer.

Furthermore, the complexes **2–5** exhibit emission in the solid state at ambient temperature.

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

REFERENCES

1. F. D. Sokolov, M. G. Babashkina, D. A. Safin, A. I. Rakhmatullin, F. Fayon, N. G. Zabiroy, M. Bolte, V. V. Brusko, J. Galezowska and H. Kozlowski, *Dalton Trans.* (2007) 4693–4700.
2. M. G. Babashkina, D. A. Safin, L. Szyrwił, M. Kubiak, F. D. Sokolov, Y. V. Starikov and H. Kozlowski, *Z. Anorg. Allg. Chem.* **635** (2009) 554–557.
3. R. C. Luckay, X. Sheng, C. E. Strasser, H. G. Raubenheimer, D. A. Safin, M. G. Babashkina and A. Klein, *Dalton Trans.* (2009) 4646–4652.
4. D. A. Safin, M. G. Babashkina, A. Klein and M. Bolte, *CrytEngComm* **12** (2010) 134–143.
5. D. A. Safin, M. G. Babashkina, M. Bolte, F. D. Sokolov and V. V. Brusko, *Inorg. Chim. Acta* **362** (2009) 1895–1900.
6. N. G. Zabiroy, A. Yu. Verat, F. D. Sokolov, M. G. Babashkina, D. B. Krivolapov and V. V. Brusko, *Mendeleev Commun.* **13** (2003) 163–164.
7. A. Y. Verat, F. D. Sokolov, N. G. Zabiroy, M. G. Babashkina, D. B. Krivolapov, V. V. Brusko and I. A. Litvinov, *Inorg. Chim. Acta* **359** (2006) 475–483.
8. M. G. Babashkina, D. A. Safin, F. Fayon, A. I. Rakhmatullin, F. D. Sokolov, A. Klein, D. B. Krivolapov, T. Pape, F. E. Hahn and H. Kozlowski, *Dalton Trans.* **39** (2010) 8261–8268.
9. D. A. Safin, M. G. Babashkina, T. R. Gimadiev, M. Bolte, M. V. Pinus, D. B. Krivolapov and I. A. Litvinov, *Polyhedron* **27** (2008) 2978–2982.
10. F. D. Sokolov, M. G. Babashkina, F. Fayon, A. I. Rakhmatullin, D. A. Safin, T. Pape and F. E. Hahn, *J. Organomet. Chem.* **694** (2009) 167–172.
11. D. A. Safin, M. G. Babashkina, M. Bolte, T. Pape, F. E. Hahn, M. L. Verizhnikov, A. I. Bashirov and A. Klein, *Dalton Trans.* (2010) accepted for publication.
12. D. A. Safin, M. G. Babashkina, F. D. Sokolov, N. G. Zabiroy, J. Galezowska and H. Kozlowski, *Polyhedron* **26** (2007) 1113–1116.
13. F. D. Sokolov, V. V. Brusko, N. G. Zabiroy and R. A. Cherkasov, *Russ. J. Gen. Chem.* **69** (1999) 1006–1007.
14. N. G. Zabiroy, V. V. Brusko, A. Y. Verat, D. B. Krivolapov, I. A. Litvinov and R. A. Cherkasov, *Polyhedron* **23** (2004) 2243–2252.
15. F. D. Sokolov, V. V. Brusko, N. G. Zabiroy and R. A. Cherkasov, *Curr. Org. Chem.* **10** (2006) 27–42.
16. F. D. Sokolov, D. A. Safin, N. G. Zabiroy, A. Yu. Verat, V. V. Brusko, D. B. Krivolapov, E. V. Mironova and I. A. Litvinov, *Polyhedron* **25** (2006) 3611–3616.
17. F. D. Sokolov, D. A. Safin, M. G. Babashkina, N. G. Zabiroy, V. V. Brusko, N. A. Mironov, D. B. Krivolapov, I. A. Litvinov, R. A. Cherkasov and B. N. Solomonov, *Polyhedron* **26** (2007) 1550–1560.
18. F. D. Sokolov, D. A. Safin, M. Bolte, E. R. Shakirova and Babashkina, *Polyhedron* **27** (2008) 3141–3145.
19. D. A. Safin, M. G. Babashkina, M. Bolte and A. Klein, *Polyhedron* **28** (2009) 1403–1408.
20. D. A. Safin, M. G. Babashkina, F. D. Sokolov, S. V. Baranov, F. E. Hahn and T. Pape, *Z. Anorg. Allg. Chem.* **635** (2009) 1613–1619.
21. R. C. Luckay, X. Sheng, C. E. Strasser, H. G. Raubenheimer, D. A. Safin, M. G. Babashkina and A. Klein, *Dalton Trans.* (2009) 8227–8236.
22. M. G. Babashkina, D. A. Safin, A. Klein and M. Bolte, *Eur. J. Inorg. Chem.* (2010) 4018–4026.
23. A. Kaltzoglou, P. J. Cox and P. Aslanidis, *Inorg. Chim. Acta* **358** (2005) 3048–3056.
24. A. Vogler and H. Kunkely, *Coord. Chem. Rev.* **230** (2002) 243–251.

SAŽETAK

Kompleksi bakra(I) s N-tiofosforiliranom bis-tioureom [CH₂NHC(S)NHP(S)(O*i*Pr)₂]₂ i fosfinima (PPh₃, Ph₂P(CH₂)_{1–3}PPh₂, Ph₂P(C₅H₄FeC₅H₄)PPh₂): raznovrsne strukture i luminiscencija

Damir A. Safin, Maria G. Babashkina i Axel Klein

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

Rekcijom kalijeve otopine [CH₂NHC(S)NHP(S)(O*i*Pr)₂]₂ (**H₂L**) s [Cu(PPh₃)₃] ili smjesom CuI i Ph₂P(CH₂)_{1–3}PPh₂ i Ph₂P(CH₂)_{1–3}PPh₂ ili Ph₂P(C₅H₄FeC₅H₄)PPh₂ u vodenoj otopini EtOH/CH₂Cl₂, dolazi do nastajanja binuklearnih kompleksa [Cu₂(PPh₃)₂L] (**1**), [Cu₂(Ph₂PCH₂PPh₂)L] (**2**), [Cu₂{Ph₂P(CH₂)₂PPh₂}₂L] (**3**), [Cu₂{Ph₂P(CH₂)₃PPh₂}₂L] (**4**) or [Cu₂{Ph₂P(C₅H₄FeC₅H₄)PPh₂}₂L] (**5**). Strukture kompleksa istražene su IR, ¹H i ³¹P{¹H} NMR spektroskopskim metodama, a sastav istih ispitan je mikroanalizom. Također, istražena su luminiscentna svojstva kompleksa **1–5** u krutoj fazi.